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STUDIES ON PROPERTIES OF POTATO GRANULES AND THEIR PROCESSING TECHNIQUES

BY

© KABIR HUSSEIN MOLEDINA

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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ABSTRACT

Scanning electron microscopy (SEM) was used to study the microscopic changes and to obtain information on surface structure of potato cells as affected by the commercial "Add-Back" (A-B) and the "Freeze-Thaw" (F-T) processes for potato granule production. The information was then related to other data on granule processing and end-product quality. A comparison of the two processing methods and the resulting products was made. The SEM study revealed that freezing of mashed potatoes in the F-T process greatly accelerated the rate of drying in subsequent steps by increasing the porosity of the starch matrix and the cell wall through ice crystal formation. The resultant granules reabsorbed water at a faster rate and more consistent ratio than the A-B granules.

The significance of precooking was studied with potato tissue and model systems (purified cell wall and middle lamella (CW/ML), pectin methylesterase (PME), and major tuber cations). Steam-cooked potatoes receiving a precooking (70°C) and cooling treatment were firmer and showed lesser solubilization of pectic substances than those cooked without the pretreatment. Cooked potato tissue which had been precooked at 70° or 75°C in the presence of added calcium was significantly firmer than that precooked at 65°C, indicating that PME had a limited, and possibly negative role in the firming of potato tissue.

During precooking, starch gelatinized and released calcium to form Ca-bridges with free carboxyl groups on the galacturonan. Cooling stabilized these bridges, rendering the CW/ML pectins more resistant to further thermal degradation during final cooking. The results showed that precooking and cooling were needed to produce the firm potato tissue and cell wall essential to the mash-mixing operation of the A-B

process. However, the pretreatment was found detrimental to the F-T process. The reduction in the degree of solubilization brought about by the Ca-bridges resulted in greater intercellular cohesion, causing poor cell separation and excessive cell damage on mashing. The overall process efficiency was also greatly reduced.

The batch F-T process was successfully modified to a semi-continuous one by connecting a cyclone collection system between the pre-drying, granulation and drying steps, and by varying stirrer speed, and air temperature and velocity.

Storage of the potato granules for about 33 weeks resulted in maximum retrogradation and water holding capacity, and minimum swelling. This reduced the rehydration rate and improved the extrusion properties of the dough made from granules.

An Automash machine was successfully adapted to reconstitute the granule mix for the production of extruded French fries. A uniform dough could be produced with the modified technique. The formula developed for the extruded French fries was well accepted by taste-panels.

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INTRODUCTION

Potatoes provide 25% of the world's food from plants and are a staple in the diet of many people. Dehydrated instant mashed potato granules are becoming increasingly accepted, especially with the convenience-food oriented society in the Western Hemisphere. This has led to the development of various processes for the manufacture of the granules, the so-called Add-Back (A-B) process being the most successful commercially (Boyle, 1967). A pilot-scale Freeze-Thaw (F-T) Process, introduced by Ooraikul (1977), had numerous advantages over the A-B process. The F-T process is simple to operate and control, and requires simpler and smaller equipment to produce the same amount of product. The latter advantage is met by eliminating recycling of 85-90% of the dry product, a major feature of the A-B process. The granules obtained by these two processes differ in their physicochemical characteristics. The reconstituted mashed potatoes from the F-T granules are superior in textural quality, and both the flavour and colour of the product resemble those of freshly mashed potatoes (Ooraikul, 1974). However, more development is necessary before the F-T process can be commercially feasible.

One of the essential features of the A-B process is that potatoes are precooked in water at 65-80°C for 20-30 min, and cooled before they are cooked for further processing (Cording and Willard, 1954; Olson and Harrington, 1955). The exact nature of the precook treatment is still not well understood. However, the most important effect is that potatoes have a firmer texture than those not precooked (Bartolome and Hoff, 1972b; Potter et al., 1959; Reeve, 1967). The precooking treatment improves the quality of A-B granules (Cording and Willard, 1957), but its

effect on the F-T process has not been studied.

Recently, there has been an increasing demand for potato granules for the manufacture of snack products. One such use is the production of extruded French fries. Fries made with a French fry potato mix have a number of advantages, including dry storage of the mix, 90 sec frying time, reduced shrinkage, up to two hour holding time after frying, and year round uniformity of the product (Jadhav et al, 1976). However, extruded French fries have not been commercially successful due to reconstitution and handling problems, which have resulted in fries having a ragged appearance, a tendency to stick or crumble during frying, excessive imbibition of oil, and unacceptable texture and eating qualities. Some of these problems are common in the manufacture of other snack products having potato granules as a major ingredient. Indeed, secondary uses for the granules would increase if these problems could be solved.

OBJECTIVES OF THE INVESTIGATIONS

The main objective of the present work was to understand some of the factors related to the Freeze-Thaw and the Add-Back techniques and the product they produce, and in particular to elucidate the nature of the precook treatment. Another purpose was to develop a better formula and reconstitution technique for extruded French fries to obtain a product with improved texture and eating quality, and freedom from oiliness. The following areas were chosen for detailed study:

2.1. Structural changes in potato tissue during processing as viewed by scanning electron microscopy.

Physical properties of foods are very often correlated with their submicroscopic structure. Therefore, scanning electron microscopy (SEM) was used to characterize the structural changes in the potato tissue that occur during each of the steps in the A-B and the F-T processes. The information obtained could reveal weaknesses and advantages of each process so that they might be corrected and optimized.

2.2 Effect of the procook treatment in the F-T process.

The exact nature of the precook treatment, which has a profound effect on the quality of the A-B granules, is not well understood. It was advisable to determine the effect and usefulness of the precook treatment in the F-T process. This portion of the studies included firmness measurement of intact tissue, firmness and glueyness measurements of freshly mashed and reconstituted mashed potatoes, changes in water- and calgon-soluable fractions of pectic substances, and SEM studies of cooked potato tissue with and without the precook treatment.

2.3. Model studies on the role of PME, cations and starch in the firming effect of the precook treatment of potato tissue.

A study with model systems consisting of purified potato cell wall, pectin methylesterase (PME), starch and major cations in the potato tuber was undertaken to clarify the roles of these potato constituents in the firming effect induced by precooking. PME was extracted from potato tissue and its pH and temperature optima were determined. The degree of pectin demethylation and solubilization as affected by PME, Ca^{2+}, Mg^{2+} and starch during precooking and cooling were evaluated. The effect of added Ca^{2+} on tissue firmness was also determined in situ.

2.4. Further development of the F-T process.

The F-T technique has several advantages which indicate that it could become accepted in the industry. It is desirable to study the processing parameters in detail and then modify the batch process to a semi-continuous one. Such information would be very useful in designing a continuous process of pilot or commercial scale, and would enable the control of processing conditions so that the final product could be modified to meet any usage requirements set by customers. Studies of the processing parameters were conducted under batch operation to determine optimum processing conditions with respect to the temperature of the thawed mash for efficient predrying, the moisture content of the predried product for efficient granulation, variation of raw material, and efficient stirrer design. Under a semi-continuous operation, the processing parameters studies were air velocity, temperature and the time optima for predrying, granulation and final drying.

2.5. Physiciochemical changes during aging of potato granules.

A major drawback of extruded French fry production is the rapid rehydration of the mix, resulting in a non-uniform dough that cannot be handled or extruded properly and yields fries of poor eating quality. Granules which have been aged formore than six months do not suffer from this disadvantage, but do present a rancidity problem. A study was undertaken to understand the physicochemical changes occurring during the aging process and to relate these changes to the rehydration rate of the granules and the extrusion properties of the dough. Characteristics investigated included rehydration rate, extrudability, degree of retrogradation, moisture content, and swelling power.

2.6. An improved process for extruded French fry production.

The foregoing problems have prevented market acceptance of extruded French fries. Attempts to accelerate the physicochemical changes of fresh granules and hence, lower the rehydration rate of the granules were unsuccessful. Studies were redirected to the improvement of the reconstitution method and the formulation of the mix. These studies included the modification of the commercially available automatic mash pototo reconstitution equipment for French fry mix reconsitution, and the development of better formulae for the mix.

REVIEW OF THE LITERATURE

3.1. PROCESSING TECHNIQUES FOR POTATO GRANULE PRODUCTION.

The potato, Solanum tuberosum L., is a very important component in the diet of many people. Recent advances in the food industry have made potatoes available in many processed forms, the convenience and the quality of which attract more consumers and higher consumption (Boyle, 1967).

Among the dehydrated products, dehydrated mashed potatoes, comprised of flakes and granules, have become widely accepted in both consumer and institutional markets (Feustel et al., 1964). Potato granules are dehydrated precooked potatoes in granular form that can be easily reconstituted to mashed potatoes by mixing with hot liquid (Boyle, 1967). Various methods have been developed and many patents have been issued concerning techniques and equipment used for the production of potato granules. Basic information related to potato dehydration was given by Feustel et al. (1964). Early technological development of potato granules has been adequately reviewed by Olson and Harrington (1955), Gutterson (1971) and Ooraikul (1973). Recent patents were reviewed by Torrey (1974), Hanson (1975), and Hadziyev and Steele (1978). Therefore, only a brief review of these processes is given here. However, the A-B and the F-T processes, the subjects of the present investigation, will be discussed in more detail.

Potato granules were first developed in England during World War II, and then introduced into the United States for home use in 1947 (Feustal et al., 1964). The "Freeze and Squeeze" method (Greene et al., 1949), spray drying (Rivoche, 1951a, b), and solvent extraction (Heisler et al., 1953), were among the first patented techniques to

produce granules. Rendle (1945), Willets and Rendle (1948), and Rivoche (1950), described in their patents the "First generation" A-B process which required recycling of substantial amounts of the previously dried granules to mix with freshly cooked potatoes. Hendel et al. (1962a, b) patented a direct method for processing granules without recycling of the dry seed. This was achieved by predrying the cooked potatoes to a suitable moisture level prior to conditioning at low temperatures, and granulation. Carlson and Evans (1970) patented a method and equipment for comminuting and drying of cooked potato. Vigerstrom and Strid (1974) preheated sliced potatoes prior to other conventional A-B steps. A patent by Shatila and Terrell (1976) produced granules without employing precooking and cooling steps. Partially mashed steam-cooked potatoes were priced in the presence of glycerol monostearate in order to coat the surfaces of the separated cells. The additional steps were predrying, granulation, and fluid-bed drying. During the process, amylose solubilized but did not retrograde, giving an end-product capable of high cold water absorption. A F-T process which also omitted precooking and cooling steps was patented by Shub and Bogdanova (1976). Sliced tubers were steam-cooked and mashed, and the moist mash was forzen at -10 to -40°C for 2 to 5 min. The product was then fluid-bed dried to 8-12% moisture. The ruptured cell count was 3.6%.

3.1.1. The Add-Back Process.

This process is probably the only one used for commercial-scale production of potato granules (Boyle, 1967), and is described in detail by Cording and Willard (1957) and Olson and Harrington (1955). Its basic features are: peeling, slicing, sulphiting, water-blanching (precooking), and water cooling; followed by steam-cooking, mash-mixing

with recycled granules, conditioning, remixing, air lift drying, fluid-bed drying, and cooling and sieving. In an excellent review, Hadziyev and Steele (1978), give the following rationale for the sequence of the processing steps. Slicing ensures effective and uniform heat transfer in subsequent cooking. Precooking and cooling avoids sloughiness during cooking and imparts the firmness to cell walls which is required to withstand the mechanical forces involved in the mash-mixing step. Cooking brings about final softening of the tissue. Hot mash-mixing results in tissue separation into individual cells or their aggregates, with minimum cell rupture. The conditioning step in a stream of cold air is needed to equilibrate the mash moisture content and, by keeping the moisture content above approximately 30%, forces the free starch to retrograde and thus increase the friability of the moist mash. Remixing or "fluff-mixing" is done in order to further granulate the moist mash into essentially single cell particles. This and the previous mash-mixing step are prerequisites for the moist granules to remain separated and to be conveyed and dried in subsequent air lift drying step. The latter step reduces the moisture content of the granules from approximately 30% to approximately 15%, while the following fluid bed drying further decreases the moisture content to approximately 7%. The cooled granules are then sieved. A small portion of the granules of particle size 80 mesh or less is collected as end-product, while the rest is recycled. Particles of 10 mesh or greater are removed as rejects.

Though the A-B process has been improved, its basic feature, recycling of substantial amounts (85-90%) of the previously dried granules (Gutterson, 1971), has proven to be its major disadvantage. Recycling means repeated mechanical handling and heat treatment.

Consequently there ia a high proportion of damaged cells, deterioration of the chemical and nutritional quality of the product, and possible extended microbial contamination. This has a bearing on the size and cost of operation. It also affects the product quality because undesirable characteristics, once developed, remain in the system (Hadziyev and Steele, 1978).

3.1.2. The Free-Thaw Process.

A direct technique for the production of potato granules, using a freezing and thawing step as an integral part of the process, was developed by Ooraikul (1973) and later patented (1977). The process consists of peeling, cooking, mashing, freezing and thawing, predrying, granulation, drying, cooking and sifting.

The development of the F-T process was based on the findings of Greene et al. (1948), and Harrington et al. (1951), that freezing cooked potatoes caused a remarkable toughening of the cell wall and a freezing-out of water from the gelatinized starch. Subsequent thawing results in the formation of free moisture, about 50% of which can easily be expressed, leaving undamaged potato cells of a firm structure. Potter (1954) attributes these phenomena to retrogradation of the starch gel brought about by low temperature treatment of cooked potatoes. This in turn reduces the swelling capacity of the gelled starch and influences its textural properties (Reeve, 1969).

Major advantages offered by the F-T process are: Recycling of dry granules is not required, thus the size of the plant to produce similar quantity of granules is substantially smaller than an A-B plant. The predrying step of the F-T process operates under a constant rate of drying, hence, a rapid reduction of moisture from about 75% to

about 45% can occur (Ooraikul, 1978). Microbial contamination is minimized due to the elimination of recycling and the use of relatively low temperatures throughout the process. Low temperature treatment also favours high retention of nutrients, especially ascorbic acid, in the F-T granules (Jadhav et al., 1975), as well as the general organoleptic properties of the product (Ooraikul, 1974). The F-T process will be discussed in greater detail under Section 3.2.

3.2. EFFECT OF PROCESSING ON POTATOES.

Potato granules are cooked and dehydrated potatoes consisting largely of spearated, whole cells (Potter, 1954) that can be quickly reconstituted to mashed potatoes by mixing with hot liquid (Feustel et al., 1964). In raw potatoes before processing, the cells are firmly connected to each other by intercellular cement, i.e., middle lamella. Each cell is surrounded with a wall, the thickness of which varies from 0.52 to 1.05 μm (Reeve et al., 1973). It was reported (Hoff and Castro, 1969) that potato parenchyma cell walls contain 28% cellulose, 55-60% pectins, 7% hemicellulose, and 5-10% polysaccharides.

The main component within the potato cell is starch in the form of starch granules which have a radial fibrial structure (Sterling, 1974). Starch comprises between 65-80% of the dry weight of the potato tuber and is calorically an important nutritional component (Schwimmer and Burr, 1967).

It is generally recognized that improvement of product quality of dehydrated potato granules is desirable. Ooraikul (1973) showed that texture largely determined the acceptance of instance mashed potatoes. Much developmental work has been directed toward improvement of the texture of the reconstituted product (Cooley et al, 1954; Olson and

Harrington, 1955; Cording and Willard, 1957; Harrington et al., 1959; Ooraikul, 1977). Texture after reconstitution is closely related to the broken cells in the product, the number of which depends, among other factors, on processing conditions and equipment used in the manufacture.

Mechanical damage to the potato cell should be avoided throughout the process to minimize release of free starch, which caused the reconstituted mashed potatoes to be pasty and thus inferior in texture (Neel et al., 1954). The proportion of broken cells in the granules is a relatively reliable indication of the textural quality (pastiness) of the reconstituted product (Green et al., 1948; Hall and Fryer, 1953; Reeve, 1963; Ooraikul, 1973). Green et al. (1948) reported that reconstituted A-B granules with 20% broken cells were very pasty; those with 10-12% were average in pastiness; and those with 6% and lower were ranked superior. Ooraikul (1974) found that properly processed F-T granules contained less than 3% broken cells and the reconstituted product resembling freshly mashed potatoes, was superior to the A-B product.

Thus, processing of potatoes into dehydrated granules involves the separation of the tissue into single cells with minimal cell rupture. The following processing steps determine whether or not this aim will be achieved.

3.2.1. Cooking.

Cooking is the first important step in the processing of potato granules. It serves to gelatinize starch granules, solubilize pectic substances in the middle lamella (ML), and prepare the potato tissue for mashing and subsequent drying operations (Kinter and Tweedy, 1967). The

tissue cells are distended by the swollen gel and tend to separate, particularly in mealy tubers (Reeve, 1967, 1970), due to the degradation of pectic substance between and in the cell wall (CW) (Linehan and Hughes, 1969a; Bartolome and Hoff 1972b; Warren and Woodman, 1974). The heat energy is thought to disrupt or weaken some of the bonds in the protopectin molecules, resulting in an increase in the water-soluble fraction of the pectic substances (Bettelheim and Sterling, 1955; Ooraikul et al., 1974). Most of the tissue cells of potatoes do not swell greatly upon normal cooking, eventhough they may become well rounded to the point of ready cell separation (Reeve, 1967), and almost all of the CWs remain intact after cooking (Ooraikul et al., 1974).

The ideal cooking techniques are those which will produce maximum mealiness, a desired textural characteristic for mashed potatoes. Undercooking results in unmashed lumps and, subsequently, higher amounts of broken cells, while overcooking causes sloughing or excessive tissue softening and, hence, more damaged cells (Severson et al., 1955; Harrington et al., 1959; Ooraikul and Hadziyev, 1974). In the F-T process steam-cooking for about 35 min was found to offer maximum cell separation with minimum cell damage on mashing (Ooraikul, 1973).

Precooking or partial cooking prior to complete cooking has been reported to increase mealiness of the dehydrated products and to firm the potato tissue (Reeve, 1954a, c; Potter et al., 1959). It has been adopted as an integral part of the A-B process in order to improve the quality of the product (Reeve, 1969; Cording and Willard, 1957; Nelson et al., 1962).

3.2.2. Mashing.

Mashing, one of the most critical steps in the F-T process,

determines the success of subsequent processing steps and the quality of the final product. It essentially involves the application of compressive and shear forces to the cooked potatoes so that the individual cells can be separated. The amount of force applied depends largely on the resistance of the material. In the case of cooked potatoes, this depends on the binding strength between the cooked cells. This strength may be collectively described as hardness or firmness of the cooked potatoes. The strength of the CW, on the other hand, determines how much force the cells can withstand without sustaining excessive damage (Ooraikul, 1973).

Mashing at temperatures close to that of cooking results in easy separation with little damage to the CW (Ooraikul, 1973). If the cells are broken, gelatinized starch will be released, resulting in an undesirable sticky mash (Reeve, 1963; Ooraikul, 1973), which not only makes the succeeding stages of processing more difficult, but also produces an unacceptable product (Olson and Harrington, 1955; Harrington et al., 1959). Temperature of the potatoes during mashing, time, and equipment used for the purpose determine the success of this step (Ooraikul, 1973). In the F-T process mashing for about two min at a temperature not lower than 70°C in a Hobart mixer equiped with a flat beater produces optimal results.

In the A-B process, cell separation is achieved by hot mash-mixing the cooked tissue with dry granules ("seed"). The mixing serves to lower the moisture content ofthe cooked potatoes to a point where the tissue is no longer cohesive and the cells can be separated without breakage (Severson et al., 1955). Harrington et al. (1959) reported that rapid cooling before completion of the mash-mixing damages the

cells and produces a sticky mash. Thus, to minimize cell rupture, mash-mixing above room temperature was recommended. Mash-mixing involves compression and frictional forces and, hence, the potato cells must be strong in order to withstand these forces without sustaining excessive damage (Harrington et al., 1959). Cell strengthening may be achieved by various precooking treatments, a mild heat treatment being the most commonly used (Cording and Willard, 1957; Nelson et al., 1962).

Additives such as surfactants and antioxidants may also be added at this stage since mashing ensures thorough mixing.

3.2.3. Freezing and Thawing.

Freezing and thawing is perhaps the most critical step in the F-T process upon which the success of subsequent steps depends (Ooraikul, 1973). It reduces the swelling capacity of the gelled starch of cooked potatoes and influences the textural properties of the product (Reeve, 1967). As much as 50% of the water may be removed from within the cell to the outside. The resulting product is more granular and less gelatinous in texture (Rendle, 1945). A remarkable toughening of the CW occurs (Greene et al., 1948) which makes dehydration and cell separation during predrying and granulation more easily accomplished (Ooraikul and Hadziyev, 1974).

The physicochemical changes (retrogradation) occurring during freezing and thawing of the F-T process are brought about in the A-B process by a conditioning step. Conditioning at 40-50°C forces starch to retrograde and, thus, increases the friability of the moist mix (Potter, 1954). This improves cell separation in the subsequent step of fluff-mixing, and the textural quality of the reconstituted product (Severson et al., 1955; Olson et al., 1953).

3.2.4. Predrying and Granulation.

The main aim of predrying is to reduce the moisture content of the cooked potato to within a critical range of 35-45% in the F-T process (Ooraikul, 1978), and 30-35% in the A-B process (Olson et al., 1953; Harrington et al., 1959). Within the critical moisture range, potato cells are friable, more resistant to mechanical damage, and easily handled (Olson et al., 1953).

In the F-T process, predrying is achieved by passing hot air at a high velocity over the thawed mash while it is being slowly stirred over a perforated bed. Due to the granular nature of the thawed mash, drying takes place rapidly under constant rate period (Ooraikul, 1978) to reduce the moisture from about 75% to about 45%.

The purpose of granulation is to separate the predried product into mainly single cells without excessive cell damage. Granulation is another critical step in the F-T process, since the extent of cell damage, the granule size, and the percentage of fine granules taken as final product are essentially determined at this stage. Granulation in the F-T process is accomplished by applying high compression and shear forces to the partially dried potato particles for a short period of time, normally about 10 minutes.

In the A-B process, predrying and granulation are effectively achieved during the mash-mixing step. Fluff-mixing also ensures a more complete separation of cell aggregates into individual cells (Severson et al., 1955).

The above steps are directed toward one aim: to process cooked potatoes into dry, fine granules consisting mainly of single whole potato cells which, upon reconstitution with hot liquid, instantly give

mashed potatoes that possess most of the organoleptic qualities associated with freshly cooked mashed potatoes.

3.3. CHEMICAL COMPOSITION AND TEXTURE OF COOKED POTATOES.

The texture of reconstituted dehydrated mashed potatoes has a major influence on consumer acceptance (Ooraikul, 1974). The consumer expects a textural quality which resembles that of freshly cooked and mashed potatoes: mealiness, smoothness and dryness are the desirable characters, whereas, rubberiness, glueyness and sogginess are undesirable (Szczesniak and Kleyn, 1963). Undoubtedly, the textural quality of the dehydrated product will be influenced, among other factors, by the texture of the starting material, i.e., cooked potato. Hence, information concerning cooked potatoes may shed light on the textural properties of dehydrated mashed potatoes.

Structural changes that potatoes undergo on cooking provide a wide variety of textural qualities (Reeve, 1977). According to Burton (1966), "mealy" potatoes may retain their form but are easily broken down and, upon mashing, separate into essentially single cells. "Waxy" potatoes exhibit no sign of being undercooked, but may be cut into slices, and many cells will be ruptured on mashing.

The texture of cooked potato, thought to be controlled by a number of factors, has been extensively reviewed (Linehan and Huges, 1969a; Van Buren, 1970; Warren and Woodman, 1974; Keijbets et al., 1974; Reeve, 1977). A number of workers have attempted to define the mechanisms by which the various tuber constituents interact to control the texture of the cooked tuber. According to Reeve (1954 a,b,c), "mealiness" is the subjective perception of the flow characteristics of cooked tissue and potato texture is determined primarily by the starch

content. Gelling starch produces a "swelling pressure, and a tendency towards cell distension, causing them to "round off" and thus separate from one another with consequent breakdown of intercellular cohesion and disruption of the tuber. On the other hand, Bartolome and Hoff (1972a) state that the reduction in cell cohesion which occurs during cooking results from the breakdown of polyuronides in the intercellular cement (ML) of the potato cells, thus allowing spontaneous cell separation and "sloughing". A third hypothesis offered by Warren et al. (1975), ascribes the reduction in tissue strength which occurs on cooking to water uptake by the polysaccharides of the CW. There is an increase in the thickness of the CW and reduction in the viscosity of the CW matrix; both effects combining to reduce the stress required to separate cells. According to this theory, high levels of polyvalent metals in the cell wall material favour cell separation and tissue breakdown.

Calcium and magnesium may interact with the ML polyuronides and be of importance in influencing the texture of cooked potato. Firming and reduction of sloughing can be brought about by addition of Ca^{2+} and Mg^{2+} to water in which potatoes are cooked (Whittenburger and Nutting, 1950; Bettelheim and Sterling, 1955). These changes in the tuber are assumed to result from an interaction between the ions and carboxyl groups of the ML pectic substances. Clearly, only ions already present in the intercellular cement, or those free to interact with it during cooking, will be of importance in influencing intercellular cohesion (Linehan and and Hughes, 1969a).

The literature indicates that cohesion between cells is one of the main factors governing the textural properties of cooked potato tissue. Fundamentally, changes upon cooking involve starch gelatinization

and solubilization of pectic substances, resulting in separation of potato cells in the cooked tissue. There is, however, still some controversy concerning the role starch plays (Reeve, 1972) compared to that of pectic substances (Hoff, 1972).

3.3.1. Role of Pectic Substances.

Pectic substances are one of the most important classes of the naturally occurring polyuronides in plants (Rouse and Atkins, 1955). The basic structure of pectin is a polymer of a mixture of poly-galacturonic acids in which the carboxyl groups are methylated to varying degrees (McCready, 1970).

Pectic substances in the CW are part of the hemi-cellulose-pectin gel which functions both as a structural element and as a membrane (Pilnik and Voragen, 1970). Pectin in the ML acts as a cohesive agent, and so it is referred to as "intercellular cement" (Hadziyev and Steele, 1978).

Potter and McComb (1957) determined that the amount of pectic substances in potatoes was 0.7-1.5% on a dry weight basis, while Sharma et al. (1959) reported a range of 0.8-1.5% fresh weight. Bettelheim and Sterling (1955) found that the uronide content of 10 varieties was 1.1-2.1% dry weight, whereas Jaswal (1969) reported uronide contents as high as 4.5-4.8% dry weight. Hoff and Castro (1969) found that CWs were 5.0-7.2% of the potato dry weight, and that pectic substances made up 47.5-62.5% of the dry CW. This corresponded to 2.4-3.5% pectic substances in the dry tuber. Ooraikul et al. (1974) reported an apparent total content of 1.45% on dry weight basis.

Keijbets and Pilnik (1974), using a copper-ion exchange technique rather than the carbazole test of the above reports, found the galacturonan

content of the cultivar Bintje to be 2.62% dry weight for potatoes below a specific gravity of 1.060. The discrepancies in the reported uronide contents appeared to be due mainly to differences between the samples studied and the methods of analysis employed.

Pectic substances in raw tubers exist in the form of protopectin, the water-insoluble parent substance, and pectin, which is composed of water-soluble pectinic acids (McCready, 1970). Protopectin can be subdivided into two fractions. The first can be rendered water-soluble by treatment with sequestering agents, while the second is strongly bound by enmeshing with other filamentous macromolecules in the CW, and is not soluble in the presence of sequestering agents (Lineham and Hughes 1969c). It could, however, be extracted by strong acids at elevated temperature (Bettelheim and Sterling, 1955; Linehan and Hughes, 1969a).

Although the CW and ML of potato tissue constitute only a minor portion of the total solids present in the tuber, the pectic substances in the CW and ML appear to exert a profound effect on the textural properties of cooked potatoes (Linehan and Hughes, 1969a; Ooraikul, 1973). A shift from insoluble towards water-soluble pectin generally occurs upon cooking (Freeman and Ritchie, 1940; Bettelheim and Sterling, 1955; Ooraikul et al., 1974), and there is a loss of cellular cohesion of tissue (Linehan and Hughes, 1969a), implying a relationship between cohesion and solubilization of pectic substances in the CW and, in particular the ML (Northcote, 1972).

A statistically significant correlation between the amount and characteristics of extracted pectin fractions, and the intercellular cohesion retained by cooked potato tissue was reported by Warren and

Woodman (1974). Linehan and Hughes (1969b) found a significant correlation between intercellular cohesion and a pectin fraction that was soluble in a calcium sequestering agent. The fraction was thought to be responsible for the structure of the retained intercellular cement.

Changes in pectic substances, as induced by cooking of potatoes, were reported by Ooraikul et al. (1974). The content of pectic substances in raw tubers was low in both water- and calgon-soluble fractions, implying that pectic substances in the Netted Gem cultivar are mainly in tightly bound forms. However, steam-cooking brought about a sixfold increase of the water soluble fraction. The cooked potato tissue was firm, but could easily be separated in to single cells by mashing (Ooraikul, 1973). This implies that solubilization during cooking of the major portion of the CW binding components of potatoes has a significant role in tissue softening. However, the role of pectic substances in intercellular cohesion, reflecting more or less the texture of raw and cooked potatoes, is still not clear.

A few attempts to clarify the mechanism of degradation and solubilization of pectic substances during cooking were reported by Keijbets et al. (1976). In model systems consisting of purified CW, they confirmed that pectic galacturonan, at the natural pH of potato tissue (5.5-6.5), was depolymerized by β- or trans-elimination, and that the extent of depolymerization increased with increasing pH. The mechanism of the elimination reaction was clarified by Neukom and Deuel (1958) and Albersheim et al. (1960).

Woodman and Warren (1973) found that potato polyuronides generally had a low degree of esterification, and were present in

higher concentration in cortex and periderm than in interior regions. Furthermore, the exterior portion of the tuber, which tended to disintegrate upon cooking, had a lower degree of salt formation with Ca^{2+} and Mg^{2+} than the more cohesive central portion of the tuber.

The influence of pectin degradation on the texture of cooked potato tissue prompted Keijbets and Pilnik (1974a) and Keijbets et al. (1976) to investigate the effect of major potato cations, such as calcium, potassium and magnesium, and anions, such as citrate, malate, phytate and chloride, on the extent of β-elimination. The nature of the ions, rather than their concentration, was the predominant factor in stimulating breakdown of pectin at 100°C.

During cooking, potato starch calcium is transferred from the phosphate groups at C-6 of some glucose residues of amylopectin to carboxyl groups of galacturonan. In model systems of potato CW and starches, Keijbets et al. (1976) found that Ca-starches consistently decreased galacturonan solubilization, while H-starches had no influence. This implied that amylose, which leached from starch granules during cooking, did not stablize galacturonan as had been suggested by Linehan and Hughes (1969b).

3.3.2. Role of Starch.

Starch comprises between 65-80% of the dry weight of the potato tuber. It consists of two main components: amylose, which is a polydisperse polymer of α, 1-4 linked glucosyl residues with little branching; and amylopectin, which is a highly branched-chain glucose polymer in which the side chains are attached through α, 1-6 linkages (Osman and Hodge, 1976)

Various workers have correlated starch content with the textural quality of cooked potatoes. According to Whittenburger (1951) and Whittenburger and Nutting (1950), the texture of cooked potato is related to specific gravity, which in turn can be related to starch content. On the other hand, the cell size and the size of its starch grains are related to tuber size, which also correlates with specific gravity and texture (Sterling, 1966).

Several studies of cooked potato tissue (Whittenburger and Nutting, 1950; Whittenburger, 1951; Reeve, 1954a,b,c; Sterling and Bettelheim, 1955) have shown cell separation to be accompanied by "rounding off" of the cells. The walls of the adjacent cells are pushed apart once the pectic substances of the intercellular layer have been degraded to a certain extent. "Rounding off" was ascribed to cell distention resulting from swelling of gelatinized starch.

A number of workers have also attempted to show the dependence of the texture of cooked potatoes on the physical or chemical properties of starch, rather than the absolute amounts of starch. Linehan and Hughes (1969a) attempted to demonstrate relationships between texture and relative proportions of amylose and amylopectin. Bettelheim and Sterling (1955) found no such relationship, whilst Unrau and Hylund (1957) and Barrios et al. (1961) found a positive relationship.

Linehan and Hughes (1969b) postulated that migration of amylose from the starch granules to the ML and infiltration by amylose into the CW fabric results in reinforcement of the strength of the CW and ML. Thus, the amount of amylose affects cell cohesion and, hence, texture of cooked potato. However, this was not corroborated by the study of Keijbets et al. (1976). Warren et al. (1975) found that the swelling

pressure of gelled starch was not sufficient to account for the texture of cooked potato. Instead, it was suggested that sloughing of cooked tissue was due to excessive hydration of the CW which in turn favoured cell separation.

3.3.3. Interrelationship of Pectin and Starch.

Nearly all studies of potato texture have demonstrated an interrelationship between pectin and starch, and that softening of potato tissue during cooking is associated with cell separation. This implies that intercellular cohesion certainly is the most important textural characteristic of cooked potatoes. The extent of the loss of intercellular cohesion is also important. Excessive loss of intercellular cohesion is undesirable in potatoes which are consumed fresh, as well as in those which are processed, since sloughing represents an economic loss. On the other hand the tissue must be loosened sufficiently for easy separation into single cells during the mashing stage of granule production.

Texture of cooked potato is obviously influenced by numerous factors. The data currently available are inadequate in terms of a coherent concept for the texture of cooked potato. However, a review of the literature indicates that textural qualities of potatoes depend upon changes in both pectic substances and starch.

3.4. PRECOOKING AND FIRMING OF POTATOES.

It is well known that the degree of cell rupturing influences the texture or consistency of cooked potatoes and their products, and that stickiness or gumminess is a direct result of exuded gelatinized starch (Reeve, 1963; Ooraikul, 1974). Hence, to produce an acceptable dehydrated potato granule product, some control of the degree of cell

rupture during processing is desirable.

In an effort to minimize cell rupture and, hence, control texture, many treatments prior to cooking have been proposed. The most commonly used method is a heat treatment in water at 65-80°C for 20-30 min followed by cooking in water at 20°C before final cooking for further processing. This precooking treatment has been reported to increase the mealiness of dehydrated products and to firm the potato tissue (Reeve, 1954b; Cording and Willard, 1957; Potter et al., 1959; Harrington et al., 1959; Nelson et al., 1962; Reeve, 1969). The firming effect of precook heating is important in ensuring piece integrity in the production of diced potato products (Reeve, 1977), and in minimizing sloughing during final cooking (Whittenburger and Nutting 1950; Whittenburger, 1951).

Textural control by precooking forms an essential feature of the A-B process for the production of potato granules (Olson and Harrington, 1955; Cording and Willard, 1957), and flakes (Nelson et al., 1962). Precooking is very important in that it strengthens the potato cells (Bartolome and Hoff, 1972b) so that they can withstand compression and shear forces during the mash-mixing step of the A-B process (Potter et al., 1959). Without precooking excessive mechanical damage to the potato CWs may take place, causing the release of free starch and resulting in a texturally inferior product (Cording and Willard, 1957; Harrington et al., 1959). Thus, precooking improves the texture of the mash and of the final product, and is important to the A-B process as a means of controlling thephysical properties of potato granules (Olson and Harrington, 1955; Cording and Willard, 1957; Potter et al., 1959). It is not known whether similar benefits would accrue to the F-T process

by this precook treatment.

3.4.1. Starch Retrogradation in Precook Firming.

It has been stated that the success of the precook treatment is due to starch (amylose) retrogradation (Potter, 1954; Potter et al., 1959) and consequent reduction of "swelling pressure" (Reeve, 1954b, c; 1967). According to this view, when potato tissue is held for sometime at moderate temperatures (50-80°C), starch retrogrades (realignment and association by hydrogen-bonding of starch molecules causing a gradual decrease in their solubility). When precooking is followed by a cooling step, the extent of regrogradation is even more profound (Potter, 1954; Reeve, 1954a, b; Harrington et al., 1959). Retrogradation reduces water absorbance and, therefore, the swelling capacity of the gel. This limits the degree to which tissue cells are distended and separated, resulting in greater firmness and reduced sloughing of completely cooked potatoes (Potter et al., 1959).

3.4.2. Pectin Methylesterase and Metal Bridging in Precook Firming.

More recent work (Bartolome and Hoff, 1972b) indicates that the increase in intercellular cohesion by the precooking treatment is due to pectin methylesterase (PME, E.C. 3.1.1.11) activity. These workers found that the heat during precooking destroys the integrity of plasmalemma, permitting intracellular electrolytes to diffuse to the CW, thereby causing PME to desorb. The desorbed and activated enzyme acts on methyl ester groups of the galacturonan chains to produce free carboxyl groups. Finally, diffusion of Ca^{2+} and Mg^{2+} develops cross-linkages between the de-esterified chains, and renders the pectic substances more resistant to further thermal degradation. This would reduce the loss of intercellular cohesion and, thus, contribute to

firming and tendency of sloughing of the cooked tissue.

Warren and Woodman (1974) gave a different interpretation of the involvement of pectic substances and PME in tissue firming induced by the precook treatment. They stated that the increase of Ca^{2+} and Mg^{2+} ions bound to the de-esterified polyuronide, brought about by PME demethylation, would decrease water uptake on cooking. This reduces the overall loss in cell cohesion by lessing the increase in CW and ML thickness, and the reduction in viscosity of the pectin matrix.

PME is widely distributed in higher plants (Lineweaver and Jensen, 1951) and is associated with the de-esterification of pectic substances in the tissue (Kertesz, 1955). It is difficult to study the action of PME in situ. Consequently, research has dealt primarily with ascertaining in vitro the response of PME to various chemical and physical conditions. These studies have included determinations of the effect of salt concentrations, pH and temperature. NaCl, the most widely used salt, promotes maximum activity of PME at concentrations of 0.15-0.2M in a pH range of 7-8 (Kertesz, 1955; Rouse and Atkins, 1955; Vas et al., 1968).

Although the functions of PME in plant tissues have not been fully elucidated, there are reports which indicate that PME demethylates component pectic substances of plant tissues under certain conditions and, hence, enhances firmness of the tissue in the presence of polyvalent cations by rendering the pectic matrix less susceptible to attack by polygalacturonases and to thermal degradation (Kertsz, 1955; Rouse and Atkins, 1955; Van Buren et al., 1962; Deshpande et al., 1965; Bartolome and Hoff 1972a, b; Keijbets et al., 1976).

Deshpande et al. (1965) studies the effect of heat treatments and polyvalent cations on the texture of canned tomatoes. They showed

that tomatoes subjected to mild heat reacted more favourably with cations than non-heat treated tomatoes and hence, were firmer. This condition was ascribed to enzymatic action, resulting in some de-esterification during the mild heating. Bartolome and Hoff (1972b) offer a similar explanation for the firming of potatoes during precook heat treatment.

PME is present in potato tubers and is associated with demethylation of pectic substances. Since PME is usually bound to water-insoluble cell constituents, particularly those of the CW (Bartolome and Hoff, 1972b), it is freed by solubilization with NaCl at a pH of 7.5. The PME activity of a potato slurry was determined by Vas et al. (1968) and Bartolomé and Hoff (1972a). Hadziyev and Steele (1978) explained that an instant mashed potato process patented by Cole (1965), in which precooking was done in a phosphate buffer, appeared to rely on pH optimum activity of PME to provide dehydrated flakes of superior texture.

Bartolome and Hoff (1972b) demonstrated that PME in potato was not appreciably active until the tissue was heated to temperatures about 50°C, whereupon PME reacted with the pectins of the CW. At 60°C the enzyme activity was halved, while above 70°C it was found to be rapidly destroyed. This evidence was consistent with the preheating treatment of not only cell wall preparations, but also of potato tissue heated in the region of 60-70°C, then boiled for 30 min. There was consistent firming of the potato tissue. During preheating Ca^{2+} and mg^{2+} contents increased within the CW, but decreased in gelatinized starch.

Keijbets et al. (1976), however, showed that Ca^{2+} but not Mg^{2+} ions had the ability to stabilize the pectic galacturonan in potato CW. The activity towards Ca^{2+} increased as the de-esterification of pectic

galacturonan increased, suggesting that precooking might involve an important de-esterification reaction (Hadziyev and Steele, 1978).

The interaction of Ca^{2+} ions with pectic substances in the precooking step of a flake process and its beneficial effect on texture would appear to be one of the bases of a process patented by Nelson et al. (1962), although the authors did not fully explain the details. Essentially, the content of the patent is as follows: Potato slices were precooked for 15-45 min at 60-77°C in demineralized water containing about 35 p.p.m. Ca^{2+}. After cooling in water free of all minerals but Ca^{2+}, the potatoes were steam-cooked, mashed , and rapidly drum dried. The reconstituted product had good texture, flavour, and colour. Use of demineralized water without Ca^{2+} in precooking resulted in a pasty product.

The foregoing would suggest that PME de-esterification and metal-bridge formation have an important role in the tissue firming of potatoes during precooking. However, the exact nature of the precook treatment is still not well understood and controversy still exists between the influence of starch retrogradation (Reeve, 1972; Potter et al., 1959) and pectin solubilization (Hoff, 1972) in preheating firming and final texture of potatoes. Nevertheless, as stated by Hoff (1973), the truth probably lies somewhere between these two opposing views. Whatever the mechanism, precooking, cooling and subsequent cooking gives potatoes a firmer texture than those not precooked (Bartolome and Hoff, 1972b; Potter et al., 1959). Such a treatment is essential in the production of A-B granules of acceptable quality (Cording and Willard, 1957; Harrington et al., 1959).

3.5. PHYSICOCHEMICAL PROPERTIES.

Studies of the physicochemical properties of foods are useful in providing evidence on subtle details of macromolecular structure not obtainable by ordinary chemical and physical procedures. Properties of interest in the present investigation include retrogradation, swelling power, and water holding capacity of potato granules.

3.5.1. Retrogradation.

Retrogradation is a process whereby starch in the dissolved or hydrated state reverts to a water-insoluble form. Retrograded starch is microcrystalline and normally exhibits the β-type of X-ray diffraction pattern (Foster, 1965). Retrogradation is, therefore, the result of an attempt towards crystallization on the part of large, unwieldy molecules (Leach, 1965), and involves interaction between nieghbouring molecules, mutual alignment, explusion of water, and formation of new intermolecular forces (Foster, 1965).

The formation of intermolecular association of starch molecules, probably through hydrogen bonding between hydroxyl groups, may be considered as the formation of crystal nuclei on which additional segments of starch molecules may be deposited slowly to form crystalline regions of increasing size (Osman, 1972). The bulk of the water in the gelled starch is held in the spaces formed by the network of the gel and precipitated amylose. As the degree of association increases during aging, the gel shrinks, causing some of the water to seep from the interstices. This is known as "syneresis". The remaining water is bonded to the first layer of firmly bound water (Charley, 1970).

Of the many factors that influence retrogradation, the most important are the concentration of amylose, the length and state of

dispersion of the linear chains, temperature, and cation, anion and hydrogen ion centration (Leach, 1965). It has been observed that various salts of monovalent anions and cations retard the rate of retrogradation. Iodine is the most effective anion and potassium is the most effective cation (Foster, 1965).

French (1950) reported that retrogradation can take place even in the solid state (as in the staling of bread), and that retrogradation can be arrested with swelling agents by keeping above room temperature, or by removing moisture. Potter (1954), in his study of changes in the physical properties of starch in potato granules during processing, reported that, as the moisture content of potatoes decreases, the rate of retrogradation increases until there is about 30% water. Below 30% moisture, the rate of retrogradation begins to decrease until about 15% moisture where there is no further measurable change.

Although retrogradation has been widely studies (Foster, 1965; Leach, 1965; Collinson, 1968), reversal of retrogradation in gelled starch has not been reported. Only the reversal of retrogradation in the freshening of stale bread by reheating is well known. It has been suggested that amylopectin may regain part of its original character upon re-solution (Foster, 1965). During reheating moisture is re-distributed and, thus, become available for re-solution of retrograded amylopectin.

3.5.2. Swelling Power.

Due to the great number of hydroxyl groups on starch molecules, starch can absorb a considerable amount of water, especially during gelatinization. Though gelatinized starch can be dried, it will not completely regain its pre-gelatinized state upon rehydration. Neverthe-

less, dried gelatinized starch retains the ability to reabsorb large amounts of water (Hamm, 1965). In starch gels the absorbed water is immobilized in the gel network. An increase in the attraction between adjacent molecules by intermolecular hydrogen bonding, for instance, would decrease interstitial space and, hence, swelling (Hamm, 1965).

Investigations by Hellman et al. (1954) and Schoch and French (1947) on staling of bread have shown that the solubility and swelling power of starch decreases as bread stales and, also, that the rates of these changes are faster at lower temperatures and moisture levels. Potter (1954), in his study on changes in the physical properties of starch in moist potato mixes, reported that, as moisture content of the potato decreased from 43% to 28%, both starch solubility and swelling power decreased. The rate of change of these physical characteristics of the starch increased as the temperature was lowered from 50° to 5°C. He concluded that starch and its physical characteristics play an important role in the characteristics of potato granules.

3.5.3. Water Holding Capacity (WHC).

WHC is the capacity of the material to hold a certain quantity of water in the capillaries and voids of the substrate after surface adsorption. Most of this water is considered to be "free", i.e., it is not chemically or physically bound to the active sites. Thus, some foods contain a considerable amount of water. Potatoes contain 63-87% water (Schwimmer and Burr, 1967). This water is obviously immobilized in some way as it does not normally flow out when the food is cut. Yet, not all this water is true hydration water. Starch, for example, cannot bind more than 20 g of water per 100 g dry matter as true hydration water (BeMiller and Whistler, 1959), but potatoes (25%

dry matter) contain 300g of water per 100g dry matter. Starch gel can imbibe even greater amounts of water than native starch. The bulk of this water is not tightly bound to the macromolecules as hydration water, but exists as "free" water and is immobilized within the network of the food molecules.

WHC is probably the best example of the importance of immobilization of free water in foods. Therefore, changes of WHC occurring in food materials, such as during storage, are determined by the extent to which the physicochemically free water is immobilized within the microstructure of the tissue are are an indication of the structural changes that are occurring. Such structural changes may be caused by linking or loosening of linkages on a microstructural level. Linking would decrease and, loosening increase WHC (Hamm, 1965).

3.6. EXTRUDED FRENCH FRIES.

Increased development and manufacture of snack food items has diversified the use of dehydrated potato granules and flakes. These dehydrated potatoes, together with suitable additives, can be made into a dough which is then formed into desirable shapes and processed into snak food items such as extruded French fries, balls, rings and food bars. "Pringles" is the most successful of such products.

Extended French fries are produced when dehydrated potatoes and small amounts of binders are reconstituted with water to form a dough which is extruded into strips resembling conventional fries, and deep fat fried. This fabricated product has a number of advantages including dry storage of the mix, 90 sec frying time, reduced shrinkage, up to 2 hr holding time after frying, and year round uniformity of product (Jadhav et al., 1976).

Several techniques and equipment have been developed and patented for the production of extruded French fries. Fritzberg (1966) patented a process that provides a fabricated French fry in which a portion of potato flakes is toasted to reduce moisture content from 7 to 1%. Egg albumen at a level of 5% is used as a binder. A process described by Liepa (1968) uses milk solids as a binder. The process prepares a potato based dough comprising 21-46% by weight potato solids, 1-15% milk solids, and 53-73% water. Willard, Jr. and Roberts (1968) described a method for producing fabricated fries formed from a mixture of 95% dehydrated, comminuted potatoes and 5% of a thermal gelling cellulose ether edible binder.

The process described by Shatila and Beck (1971) covers agglomerates of potato particles, formed largely of individual potato cells, that are capable of rapid rehydration into a uniform homogenous dough in the absence of physical agitation. A uniform and cohesive dough was obtained when 35-55% of the total weight of the damp mix was water. Guar gum added at a level of 3% of the dry weight, was used as the binder.

Cremer (1976) patented a method for producing extruded French fried potatoes from dehydrated potato granules or flakes with a binder. The binder, comprised of 70% high amylose starch, 17% pregelatinized potato starch derivative, 9.5% tapioca starch derivative and 3.5% edible gum derivative, was blended in a ratio of 1:4 with dehydrated potatoes containing 3-5% each of dextrose and salt. One part of the above mixture was mixed with two parts cold tap water, and the resulting dough was extruded into strips and deep fat fried at 185-200°C for 75 sec.

A method for making fabricated French fries directly from freshly cooked potatoes has been developed by Weaver et al. (1974). In this

process mashed potatoes are extruded into strips and exposed to a current of hot air at 93-149°C to form a thin crust. After case hardening the product is deep fat fried and then frozen.

However, according to Cremer (1976) and Reeve (1977), no process has yet provided a product having all the desired properties. Some of these products require relatively expensive ingredients, stick together or crumble when fried, imbibe excessive amounts of frying oil and have undesirable textural and eating properties.

3.6.1. Binders in Extruded French Fries.

The essential ingredients of an extrudable French fry dough are dehydrated mashed potatoes, binding agents, and a sufficient amount of water to afford a moldable consistency. To be easily extrudable the dough must be cohesive, and this is greatly influenced by the binder material used. Many food binders are presently available and their uses have been extensively reviewed (Waldt, 1960, Ziemba, 1965; Scheffel and Klis, 1965; Glicksman, 1969; Klos and Glicksman, 1972; Hullinger et al., 1973; Andres, 1976a, b). Functional properties and characteristics of pertinent binders are briefly reviewed below.

3.6.1.1. Natural Vegetable gums.

The term "gum" has been applied to many substances, both hydrophilic and hydrophobic, that have "gummy" characteristics. Gums may function as thickeners, moisture-retaining agents, cohesive agents, syneresis inhibitors, andlubricants for extruded items (Hodge and Osman, 1976). Guar gum is a highly branched galactomannin and, therefore, disperses readily in cold water. It is compatible with starches, and forms tough, pliable films with starch and other polysaccharides through hydrogen bonding (Andres, 1976a).

3.6.1.2. Seaweed extracts.

Seaweeds are sources of several types of useful polysaccharides that have functions similar to vegetable gums. Algin, extracted from the CW of brown algae, is a linear polysaccharide composed of D-mannuronic and L-guluronic acids in varying ratios (Glicksman, 1969). Owing to its high molecular weight and linear structure, algin forms strong films. Because of the presence of hydrophilic carboxylate and hydroxyl groups, algin film resists penetration by oil and grease (McNeely, 1959). Sodium alginates have found numerous applications in the food industry where they act as binding, gel-producing or film forming agents without masking flavours (Glicksman, 1969).

3.6.1.3. Starches.

Starch in its native or modified form, is used extensively throughout the food industry as a processing aid. The functional properties of native starches are inherent in their type and botanical source. The stringy, mucilaginous character of unmodified starch pastes makes their use in foods unsatisfactory, except in a very few products in which they are used in conjunction with other starches (Hodge and Osman, 1976). This undesirable property may be eliminated by chemical modification and derivatization (Ziemba, 1965).

Amongst the various modified starches which are widely used in the food industry are cross-linked and pregelatinized starches. Cross-linking can be brought about by a number of chemical agents including phosphorus oxychloride. Cross-linked starches have better heat-resisting, cohesive and swelling characteristics than native starches (Glicksman, 1969). Pregelatinized starch is prepared by cooking and drying starch

slurries on drum dryers. The resulting material is able to reform a gel with cold liquids, without any need for heating, and is an effective binding and cohesive agent (Waldt, 1960).

High amylose starches obtained by fractionation are more resistant to cooking and swelling than the parent starches. During heating, amylose and amylopectin interlace to form a film-like network. These properties have been used in the application of high amylose starch as a binding, cohesive and coating agent (Hullinger et al., 1973).

3.6.1.4. Cellulose derivatives.

Cellulose derivatives are synthetic hydrocolloids, and are ethers in which alkyl or hydroxyalkyl groups have been substituted. By controlling the type and degree of substitution, it is possible to produce cellulose derivatives having a range of functional properties (Batdorf, 1959). The types commonly encountered in the food industry include sodium carboxymethylcellulose, methylcellulose, hydroxypropyl cellulose, and hydroxylpropyl methylcellulose. They are used as surfactants, thickeners, protective colloids, and film formers (Andres, 1976b). Their ability to form films upon thermal gelation has been used to improve the quality as well as to solve processing problems of fabricated foods (Glicksman, 1969). In extruded French fries, this film functions as a support and provides a barrier that reduces oil absorption and increases moisture retention and uniformity of colour (Sheffel and Kliss, 1965; Jadhav et al., 1976).

A major drawback in the production of extruded French fries is the rapid rehydration of the mix and formation of a non-uniform dough that cannot be handled or extruded properly, resulting in fries of poor quality (Packer and Tamara, 1976). An improved product could be made

possible with an improved binder combination and a reconstitution system that would produce a uniform dough.

3.7. SENSORY EVALUATION METHODS.

Much has been written on the methods of sensory evaluation and their effectiveness. While the use of taste panels to assess product quality parameters has inherent limitations there is often no other suitable method available (Larmond, 1970). Evaluation methods, selection and training of panelists, number of samples per session, and preparation and presentation of samples are important considerations in the organoleptic panel testing (Kramer et al., 1961).

Certain types of methods have been demonstrated to be more efficient than others. For instance, the variable multiple comparison test, in which each sample is scored on a hedonic scale, is often more informative than duo-trio or triangle tests (Kramer and Twigg, 1970; Larmond, 1970). Kramer et al. (1961) advocated that in the selection of panelists the purpose of the test is to be considered first. If the purpose is only to obtain a consumer reaction, then a trained panel is not needed, whereas for descriptive work screening and training should be conducted. The number of samples per session that can be reliably evaluated concurrently depends on the nature of the samples, the properties to be evaluated, and the skill and experience of the panelists. The major limiting factors of the panelists are sensory fatigue, boredom, and inattention(Larmond, 1970; Kramer and Twigg, 1970).

Statistical analysis is a common and most important means of evaluating the data obtained from a test panel. The importance of interactions can be determined analysis of variance. Kramer and Twigg (1970) reported that one extremely important interaction in test

panel results is the "treatment x panelist" interaction which, if significant, indicates that different panelists score the same sample differently. This means that there may be no best or worst sample but that each panelist may prefer a different sample. Caution should, therefore, be exercised when applying statistical methods for the interpretation of test panel results.

EXPERIMENTAL

4.1. SCANNING ELECTRON MICROSCOPE (SEM) STUDIES OF POTATO GRANULE PROCESSES.

4.1.1. Materials and Equipment.

Potatoes used for processing both types of granules were the Netted Gem cultivar (25±1% dry matter) grown in irrigated areas of Southern Alberta.

Glutaraldehyde. J.T. Baker Chemical Co., Phillipsburg, NJ.

K_2HPO_4 and KH_2PO_4. Fisher Scientific Co., Fair Lawn, NJ.

C_2H_5OH, purified. Fisher Scientific Co.

OsO_4. Stevens Metallurgical, New York, NY.

Liquid Freon-12. Allied Chemicals (Canada) Ltd., Edmonton, Alta.

Liquid N_2. Refrigerative Supplies Ltd., Edmonton, Alta.

Porous teflon holding thimbles.

Brass Boats, 2 cm x 3 cm x 1 cm.

Aluminium stubs.

Double-sided adhesive tape. Sellotape (Canada) Ltd.

Kodak 35 mm Tri-X Panatomic film.

Freeze-Dryer, Model FFD-42-WS. The Virtis Co., Gardiner, NY.

Cambridge Stereoscan Scanning Electron Microscope, Model 54. Cambridge Scientific Instruments Ltd., Cambridge, England.

4.1.2. Methods and Sample Preparation.

4.1.2.1. Add-Back process.

The A-B process used in this study essentially followed the outline depicted in Figure 1. Samples were taken at the following major stages from a commercial A-B granule processing plant (Vauxhall

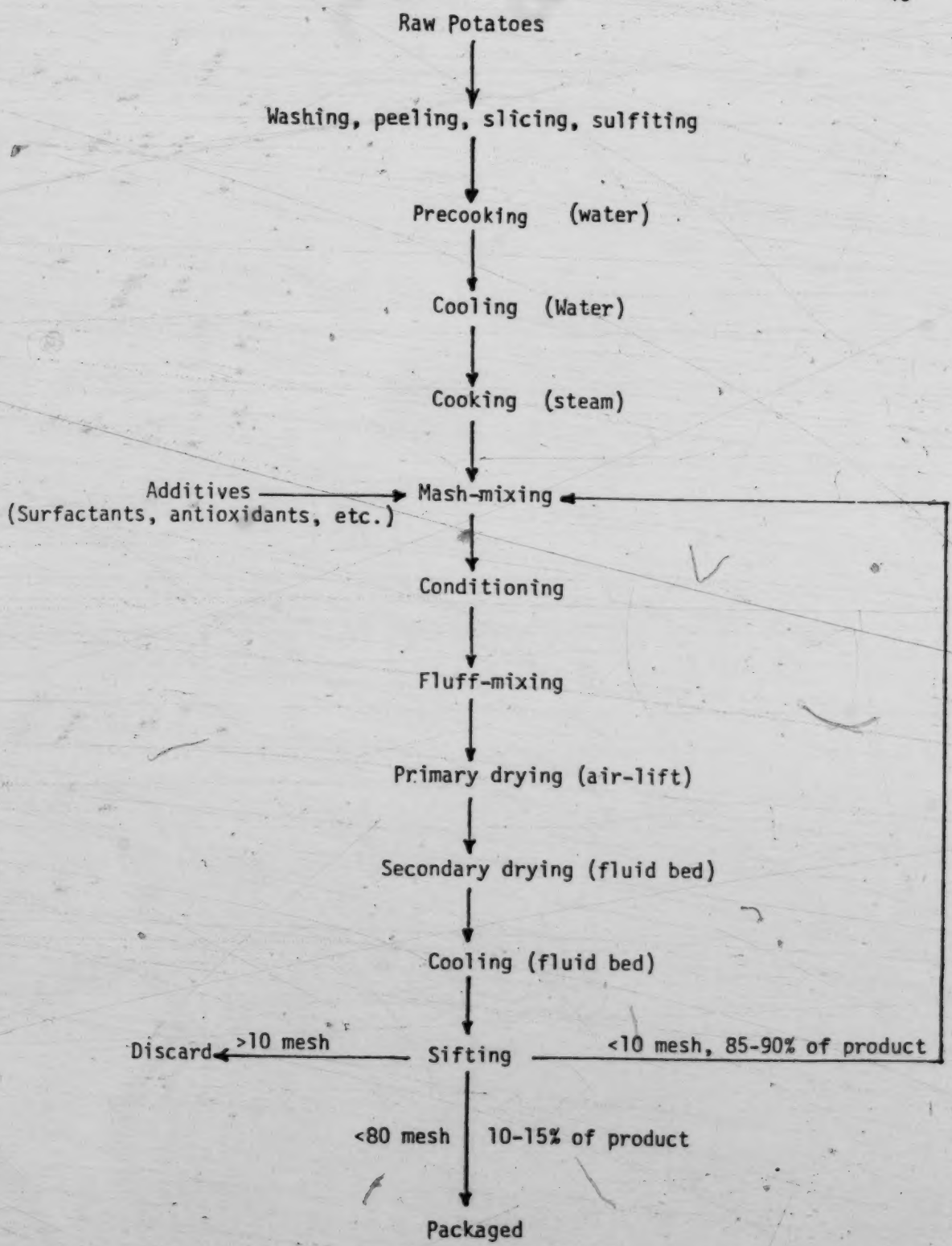


Figure 1. Flow chart of the Add-Back process.

Foods Ltd., Vauxhall, Alberta) and then were prepared for the SEM.

1. After precooking, cooling and steam-cooking.
2. At the half-way stage of the mash-mixing step.
3. At the end of the mash-mixing/beginning of conditioning.
4. End of conditioning.
5. End of fluff-mixing.
6. After air-lift drying.
7. Final packaged product.
8. Reject material ("scalp").

4.1.2.2. Freeze Thaw process.

2.5 kg mashed potatoes were processed with the F-T technique developed by Ooraikul (1973), essentially following the outline depicted in Figure 2. The following samples, taken at important stages of the process, were prepared for the SEM:

1. Steam-cooked samples, before and after mashing.
2. Frozen and thawed sample.
3. Half-way stage of the predrying step.
4. At the end of the predrying step.
5. At the end of the granulation step.
6. Final packaged product.
7. Oversized (reject) material.

4.1.2.3. Scanning electron microscopy.

Samples for SEM were prepared by the procedure outlined by Fedec et al. (1977) which was essentially as follows: Sections of about 3 mm^3 of intact tissue or about 0.5 g mashed tissue were fixed for 12 h at 4°C in 3% glutaraldehyde in 0.1 K-phosphate buffer, pH 7.0.

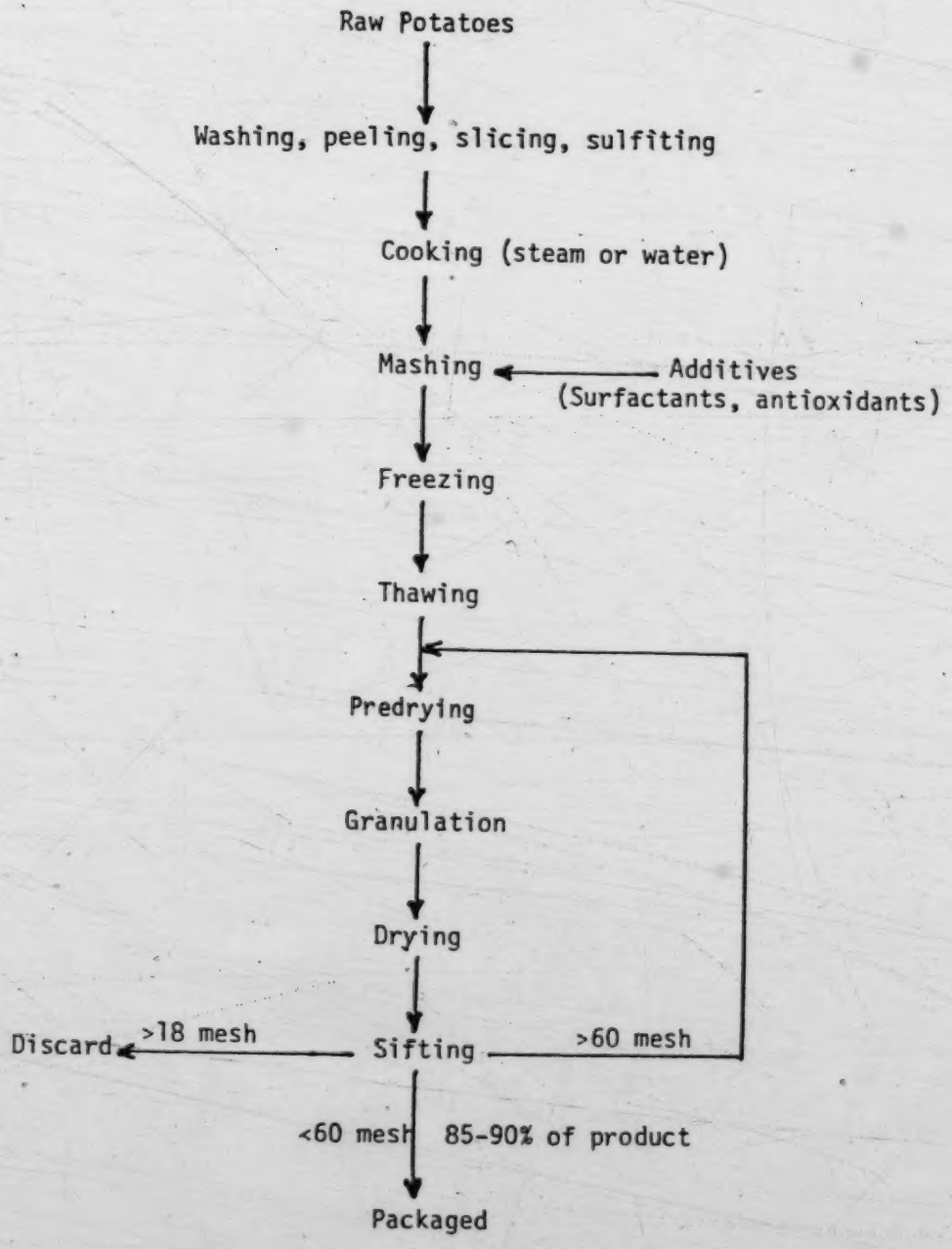


Figure 2. Flow chart of the Freeze-Thaw process.

After rinsing in buffer, the fixed samples were treated overnight at 4°C in 2% OsO_4 in the same buffer. The samples were once again rinsed in buffer and then dehydrated by successive treatments at room temperature in 50, 70, 90%, and twice, absolute ethanol.

The following procedure was adopted to maintain uniformity of treatment between potato tissue and dehydrated granules and to avoid escape of granules from the porous teflon holding thimbles. Potato granules, contained in a holding thimble, and a small quantity of OsO_4 were placed in a taped petri dish. Fixation by the OsO_4 vapours was allowed to proceed at room temperature for 12 h. The fixed samples were immersed in liquid Freon-12 that had been cooled with liquid nitrogen, and transferred into brass boats which were precooled in liquid nitrogen. The boats with the samples were then transferred into a freeze-dryer and dried overnight at -80°C. The samples were then attached to aluminium stubs with double-sided adhesive tape and coated with about 20 nm of gold. Samples were then examined by a scanning electron microscope at an accelerating potential of 15 KeV. The micrographs were photographically recorded on a Kodak 35 mm Tri-X Panatomic film.

4.2. EFFECT OF THE PRECOOK TREATMENT IN THE F-T PROCESS.

4.2.1. Processing.

4.2.1.1. Materials:

Southern Alberta Netted Gem potatoes, 25±1% dry matter content.

$NaHSO_3$. Fisher Scientific Co., Fair Lawn, NJ.

Std. Iodine Stock solution, 4.2g KI + 2.1g I_2 per 100 ml.

Myvatex type 3-50 surfactant. Eastman Kodak Co., Rochester, NY.

4.2.1.2. Equipment:

KitchenAid Mixer equipped with a flat beater. The Hobart Mfg. Co., Troy, OH.

Hobart Vegetable Slicer, Model H 4212. The Hobart Mfg. Co.

Atmospheric Steam Cooker with cover lid.

Stainless steel trays.

Air blast freezer with minimum air temperature of -29°C and air velocity of 1.42 $m^3 s^{-1}$.

Manesty Petrie Fluid-bed Dryer, Model MP.10.E., as modified by Ooraikul (1973). Manesty Machines Ltd., Speke, Liverpool, England.

Speedomax 12-point temperature recorder. Leeds and Northrup (Canada) Ltd.

Wet- (wet-wick covered) and dry-bulb (bare) temperature thermocouples.

Canadian Standard Sieve Series, and portable Sieve shaker, The W.S. Tyler Co. (Canada) Ltd. St. Catherine, Ont.

Light microscope. Leitz Wetzlar Co. Ltd., West Germany.

4.2.1.3. Procedure.

2.5 kg of potato slices were steam-cooked for 35 min with (Treatment I), and without (TreatmentII) prior precooking at 70±1°C

for 20 min and cooling in water at 18±1°C for 10 min. The cooked product was then processed with the F-T technique as described by Ooraikul (1977), with minor modifications; primarily, the temperatures of drying air were reduced. Figures in parentheses are from Ooraikul (1978): Predrying, 60-65 (93)°C, granulation, 25-32 (52)°C, final drying, 72-75 (85)°C.

The dry product was sifted for 15 min through a series of sieves ranging from 18 to 60 mesh. Particles remaining on the 18-mesh screen were considered as discard, while those passing through 60-mesh were packaged as the final product. The yield and discard were determined as a w/w percentage of the total dried product. The number of broken cells in freshly mashed and reconstituted product was assessed by examining a thin slurry in hot water under a microscope and using light iodine staining to improve the contrast of the cell boundary and the identification of unprotected starch matrices.

4.2.2. Firmness Measurement of Intact Potato Tissue.

4.2.2.1. Materials.

Ten tubers of uniform size (500±30 g).

Cork borer of 1.85 cm internal diameter.

Surgical razor-blade.

Ott-planimeter. Burrel Corp. Pittsburgh, PA.

$NaHSO_3$. Fisher Scientific Co., Fair Lawn, NJ.

4.2.2.2. Equipment.

The texturometer used to measure the firmness was developed by Ooraikul (1974). It consists of a force supplier, a signal amplifier, and a recorder.

The force supplier consists of a 0.5 hp motor with a 2.54 diameter flat-surface plunger attached to a shaft which is driven up and down vertically through a gear box at a constant speed of 14 $cmmin^{-1}$. The direction and speed of the motor is controlled by a speed controller, Model SD 14 (Minarik Electric Co., Los Angeles, CA). A system of strain gauges is mounted on a platform directly under the drive-shaft.

Signal amplifier: Daytronic Transducer Amplifier-Indicator, Model 300 D. Daytronic Corp., Dayton, OH.

Recorder: Honeywell Electronic Recorder, Model 19, with output ranges of 0.1-100 mV. Honeywell Corp., Ft. Washington, PA.

4.2.2.3. Procedure.

Ten tubers of uniform size from the same batch as that used for processing were washed, and each was trimmed to obtain a flat rectangular slab and was soaked in 0.5% $NaHSO_3$ for 1 min to prevent browning. With a cork borer, cylindrical plugs were obtained from the internal phloem region at the 8 positions shown in Figure 3. Each of the plugs was cut with a razor into two cylinders (a and b), 1.85 cm in length. The potato cylinders were washed free of starch, loosely wrapped in aluminium foil, and labelled for position identification. The first 8 cylinders (Series a) received the precooking and cooling treatment before being steam-cooked for 35 min, whereas the second 8 samples (Series b) were not pretreated.

Immediately after removal from the steam cooker, the firmness of the intact tissue was measured with the texturometer by squarely placing the hot sample flat on the load-cell platform. The plunger was driven downward onto the sample until it was compressed to 1/6 of the original height. The plunger was then immediately reversed upward

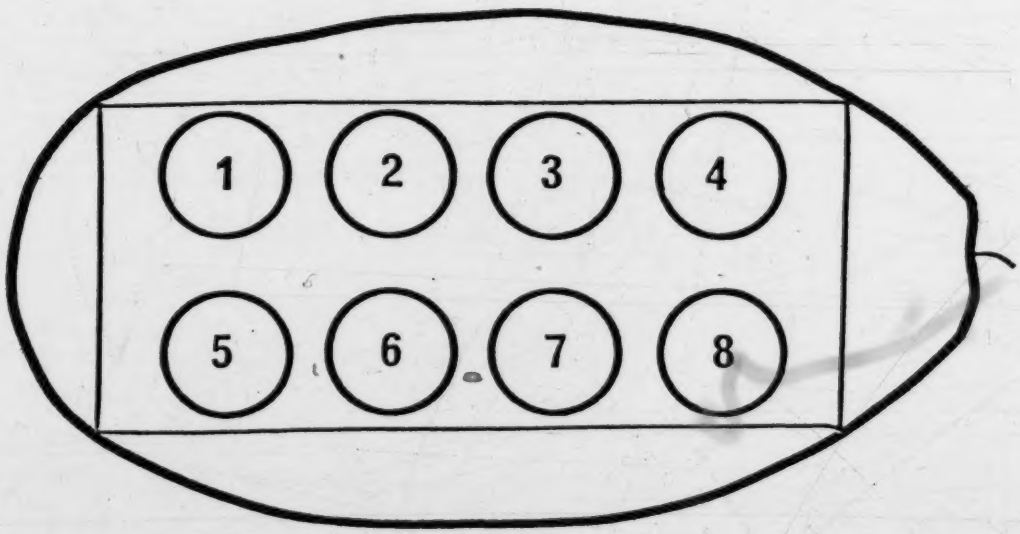


Figure 3. Diagrammetic presentation of positions where samples were taken from the potato tuber for firmness measurements.

until it was pulled clear of the sample surface. The area under the force-time surve, representing total force needed to compress the tissue, was measured with an Ott-planimeter. A paired t-test was applied to the firmness data to determine the significance of difference between Treatment I and Treatment II.

4.2.3. Textural Evaluation of Mashed and Reconstituted Potato.

4.2.3.1. Materials.

1. Precooked, cooled and steam-cooked potatoes, mashed for 1.5 min with a KitchenAid mixer equipped with a flat beater, at a speed setting of 10.

2. Treated as above, but mashed for 2.5 min.

3. Steam-cooked potatoes with no pretreatment, and mashed for 1.5 min.

4. Reconstituted potato granules (ratio of hot water to granules 4:1 v/w) processed from potatoes receiving treatment as in 1.

5. Potato granules reconstituted as in 4, processed from potatoes receiving treatment as in 3.

All samples contained 0.25% (w/v) of the surfactant Myvatex, added at the mashing stage, as recommended by Ooraikul and Hadziyev (1974).

A plastic mold of 1.85 cm internal diameter and 1.85 cm height with a fitting plunger.

A wire cheese-cutter.

Ott-planimeter. Burrel Corp. Pittsburgh, PA.

4.2.3.2. Equipment.

The strain-guage type texturometer described in Section 4.2.2.2., except that the ordinary recorder was replaced with an X-Y recorder: Moseley Model 135-A X-Y Recorder with an output range of 0.5-50 mV/in.

Hewlett-Packard Inc., Moseley Division, Pasadena, CA.

4.2.3.3. Procedure.

After the mashed potatoes had cooled to room temperature, a cylindrical sample of 1.85 cm height and 1.85 cm diameter was prepared by carefully packing the product into a plastic mold so that no unmashed pieces or air were occluded. The ends of the sample were then trimmed and smoothened with a wire cheese-cutter. The sample was carefully extruded with the aid of a fitting plunger, and placed squarely onto the center of the load cell platform. The texturometer plunger was driven downward onto the sample as described in section 4.2.2.2. The forces needed to compress the sample and to pull the plunger clear of the sample surface were recorded, and the areas of the force-time curve representing firmness and glueyness were measured with a planimeter according to Ooraikul (1974).

Four determinations were carried out using different batches of potatoes, and each measurement was done in triplicate. The data obtained were then statistically analyzed. Duncan's multiple range test was used to determine the level of difference between products receiving Treatments I and II.

4.2.4. Pectic Substances' Determinations.

4.2.4.1. Materials.

Potatoes:

Raw, Netted Gem cultivar (25±1% dry matter content).

Precooked, cooled and steam-cooked.

Precooked and cooled.

Steam-cooked.

Potato starch. Sigma Chemical Co., St. Louis, MO.

Carbazole. J.T. Baker Chemical Co., Phillipsburg, NJ.

α, D-Galacturonic acid monohydrate, reagent grade. Eastman Organic Chemicals, Distillation Products Industries, Rochester, NY.

Sodium hexametaphosphate ("Calgon"). Calgon Interamerican Corp., Consumers Division, Toronto, Ont.

H_2SO_4, conc., reagent grade. Fisher Scientific Co., Fair Lawn, NJ.

NaOH, reagent grade. Fisher Scientific Co.

Iodine, resublimed. Fisher Scientific Co.

KI, granular. Fisher Scientific Co.

C_2H_5OH, purified. Fisher Scientific Co.

4.2.4.2. Equipment.

Freeze-Dryer, Model FFD-42-WS. The Virtis Co., Gardiner, NY.

Buhler Tissue Disintegrator. Edward Buhler & Co., Tubigen, West Germany.

International Centrifuge, Model X-2, carrying a 50-ml swinging bucket type of head. International Equipment Co. Ltd., Boston, MA.

Wrist-Action Shaker. Burrell Corp., Pittsburgh, PA.

Spectronic 20. Bausch and Lomb Inc., Rochester, NY.

4.2.4.3. Procedures.

4.2.4.3.1. Preparation of samples for extraction.

Raw, precooked, precooked and steam-cooked, and steam-cooked potato samples were freeze-dried for 48 h in a Virtis freeze-dryer. The dried samples were ground for 30 min to 150 mesh with a Buhler tissue disintegrator, containing about 25 g glass beads of 6 mm diameter. The apparatus was kept cool with a water jacket at 18±1°C. The powdered samples were placed in dark, screw-capped jars and stored at 4°C until analyzed for water- and calgon-soluble fractions.

Following the procedure described in section 4.3.3.2., a starch-free preparation of CW and ML was obtained for determinations of HCl-soluble fraction and total uronide content.

4.2.4.3.2. Extraction procedure for water- and calgon-soluble fractions.

The method of Ooraikul et al. (1974), designed to minimize starch dissolution, was followed with minor modifications to extract the water- and calgon-soluble pectic substances in the potato tissue. The extraction procedure is shown in Figure 4.

4.2.4.3.3. Extraction procedure for HCl-soluble fraction.

A 0.5 g freeze-dried preparation of CW and ML was extracted with 50 ml of 0.05 M HCl at 85°C for 6 h, following the method of Bettelheim and Sterling (1955). The digest was allowed to cool to room temperature and its volume made up to 50 ml. It was then centrifuged at 1,500 x G for 15 min and the supernatant collected and designated as the HCl-soluble fraction.

4.2.4.3.4. The carbazole reaction method for analysis of uronide content of potatoes.

The method of McComb and McCready (1952), as modified by Ooraikul et al. (1974) to avoid the interference of free water-soluble starch with the carbazole reaction, was used for determining the uronide contents of the water-, calgon-, and HCl-soluble fractions. From a total of 100 ml extract, 2.5 ml aliquots were taken for determination of free starch content as described by Ooraikul et al. (1974); and 2.0 ml aliquots for determination of uronide content as described by McComb and McCready (1952). Details of the procedure are presented in Figure 5.

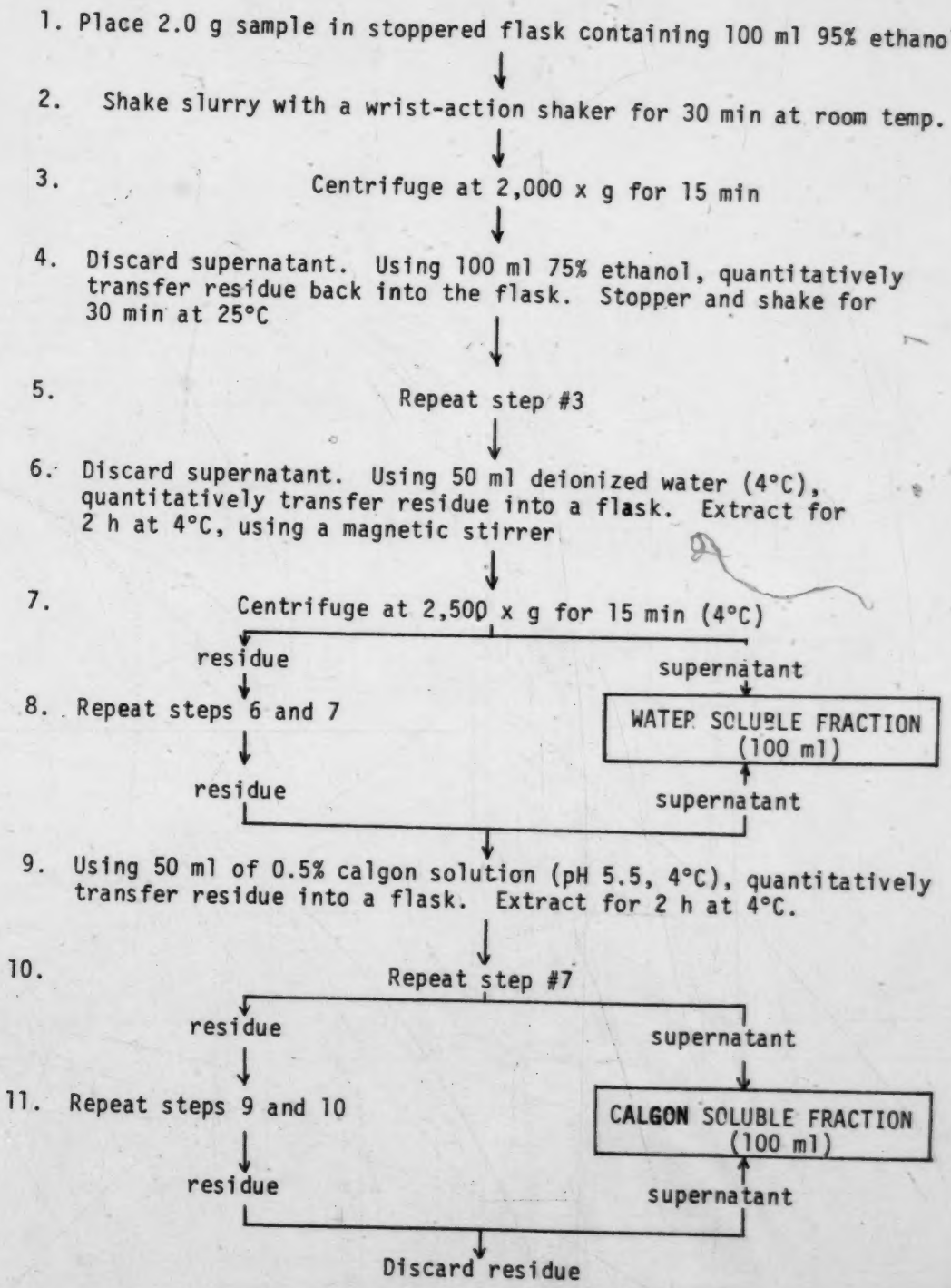

1. Place 2.0 g sample in stoppered flask containing 100 ml 95% ethanol
2. Shake slurry with a wrist-action shaker for 30 min at room temp.
3. Centrifuge at 2,000 x g for 15 min
4. Discard supernatant. Using 100 ml 75% ethanol, quantitatively transfer residue back into the flask. Stopper and shake for 30 min at 25°C
5. Repeat step #3
6. Discard supernatant. Using 50 ml deionized water (4°C), quantitatively transfer residue into a flask. Extract for 2 h at 4°C, using a magnetic stirrer
7. Centrifuge at 2,500 x g for 15 min (4°C)
residue
supernatant
8. Repeat steps 6 and 7
WATER SOLUBLE FRACTION (100 ml)
residue
supernatant
9. Using 50 ml of 0.5% calgon solution (pH 5.5, 4°C), quantitatively transfer residue into a flask. Extract for 2 h at 4°C.
10. Repeat step #7
residue
supernatant
11. Repeat steps 9 and 10
CALGON SOLUBLE FRACTION (100 ml)
residue
supernatant
Discard residue

Figure 4. A flow chart for extraction of water- and calgon-soluble pectic substances from potato.

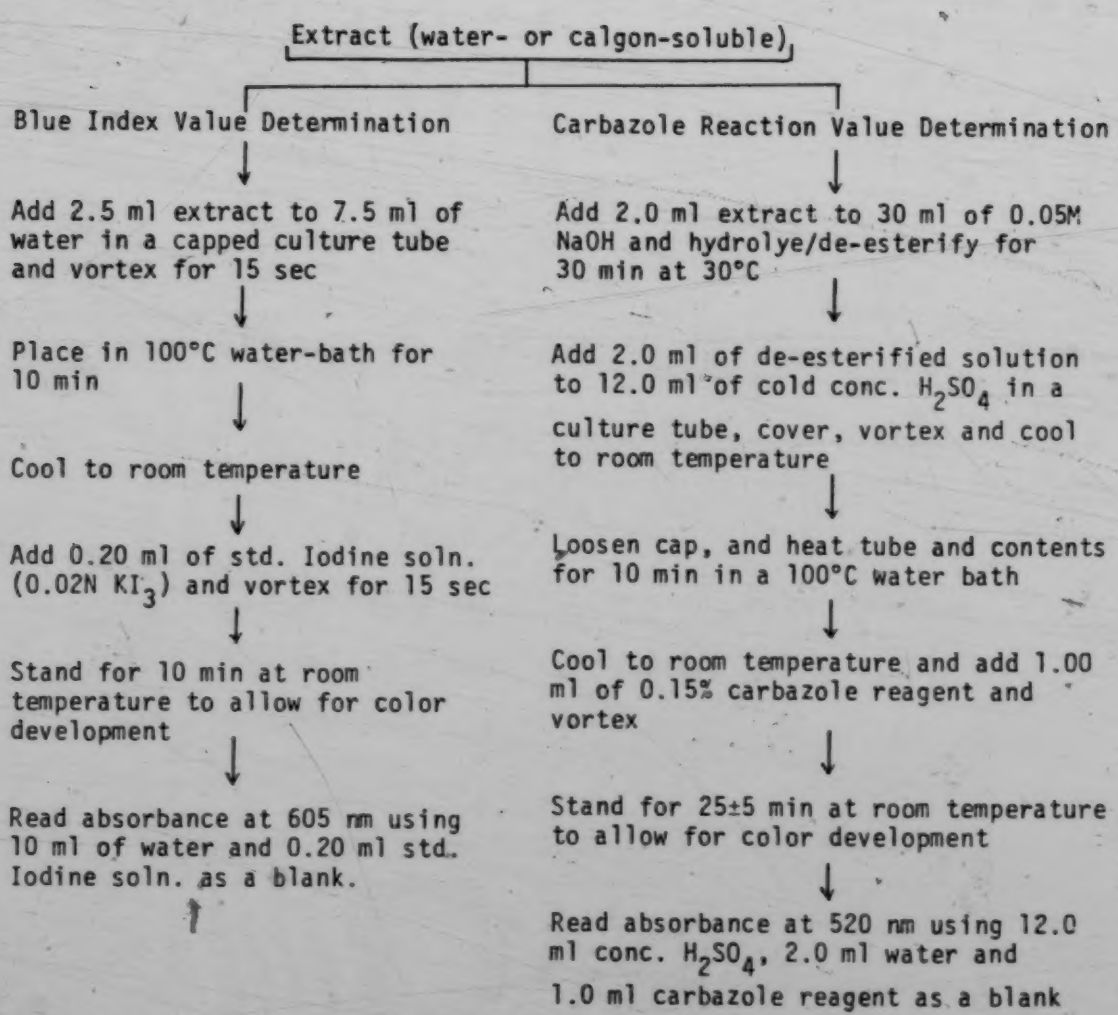

Extract (water- or calgon-soluble)
Blue Index Value Determination
Add 2.5 ml extract to 7.5 ml of water in a capped culture tube and vortex for 15 sec
Place in 100°C water-bath for 10 min
Cool to room temperature
Add 0.20 ml of std. Iodine soln. (0.02N KI_3) and vortex for 15 sec
Stand for 10 min at room temperature to allow for color development
Read absorbance at 605 nm using 10 ml of water and 0.20 ml std. Iodine soln. as a blank.
Carbazole Reaction Value Determination
Add 2.0 ml extract to 30 ml of 0.05M NaOH and hydrolye/de-esterify for 30 min at 30°C
Add 2.0 ml of de-esterified solution to 12.0 ml of cold conc. H_2SO_4 in a culture tube, cover, vortex and cool to room temperature
Loosen cap, and heat tube and contents for 10 min in a 100°C water bath
Cool to room temperature and add 1.00 ml of 0.15% carbazole reagent and vortex
Stand for 25±5 min at room temperature to allow for color development
Read absorbance at 520 nm using 12.0 ml conc. H_2SO_4, 2.0 ml water and 1.0 ml carbazole reagent as a blank

Figure 5. A flow chart for the analysis of uronide and starch contents of the potato extracts.

The uronide values of the extracts were then obtained from a standard curve (Figure 6), corrected for starch interference using a correction curve (Figure 7), as described by Ooraikul et al. (1974), and expressed as mg uronide content per 100 g dry matter. Two determinations, each done in duplicate, were carried out on four batches of potatoes, and the data were statistically analyzed.

4.2.4.3.5. Scanning electron microscopy.

The raw potato tuber was cut into halves along the minor axis. The parallel cuts obtained were sliced radially towards the centre of the pith to obtain slices of about 1 cm x 1 cm x 5 cm. Three sets of treatments were then applied to the slices, i.e., steam-cooking, precooking, and precooking and cooling followed by steam-cooking. When the samples had attained room temperature, sections of about 3 mm^3 cut from the cortical region were prepared for SEM following the procedure of Fedec et al. (1977). The mashed samples were treated similarly. Details of the SEM procedure have been described in section 4.1.2.3.

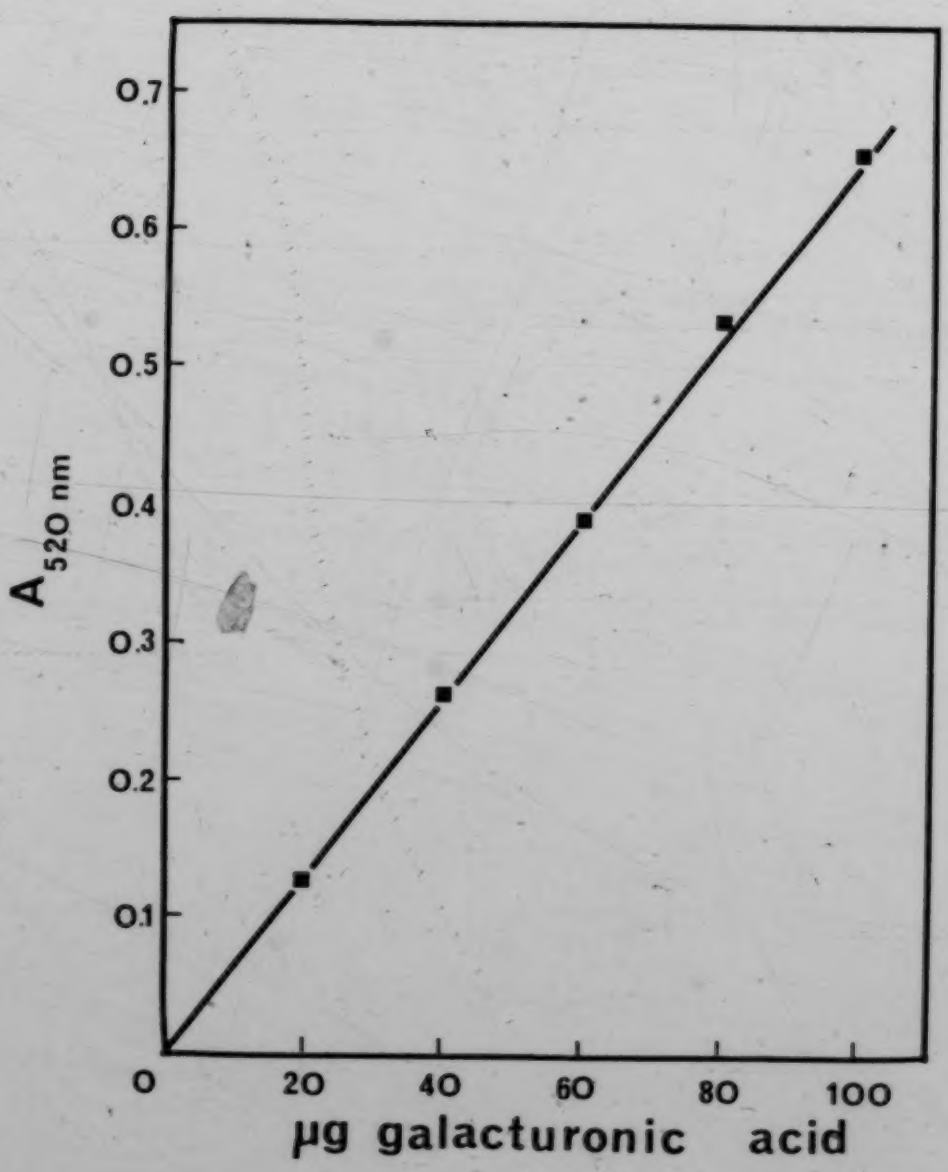


Figure 6. Standard curve of galacturonic acid monohydrate for the carbazole reaction.

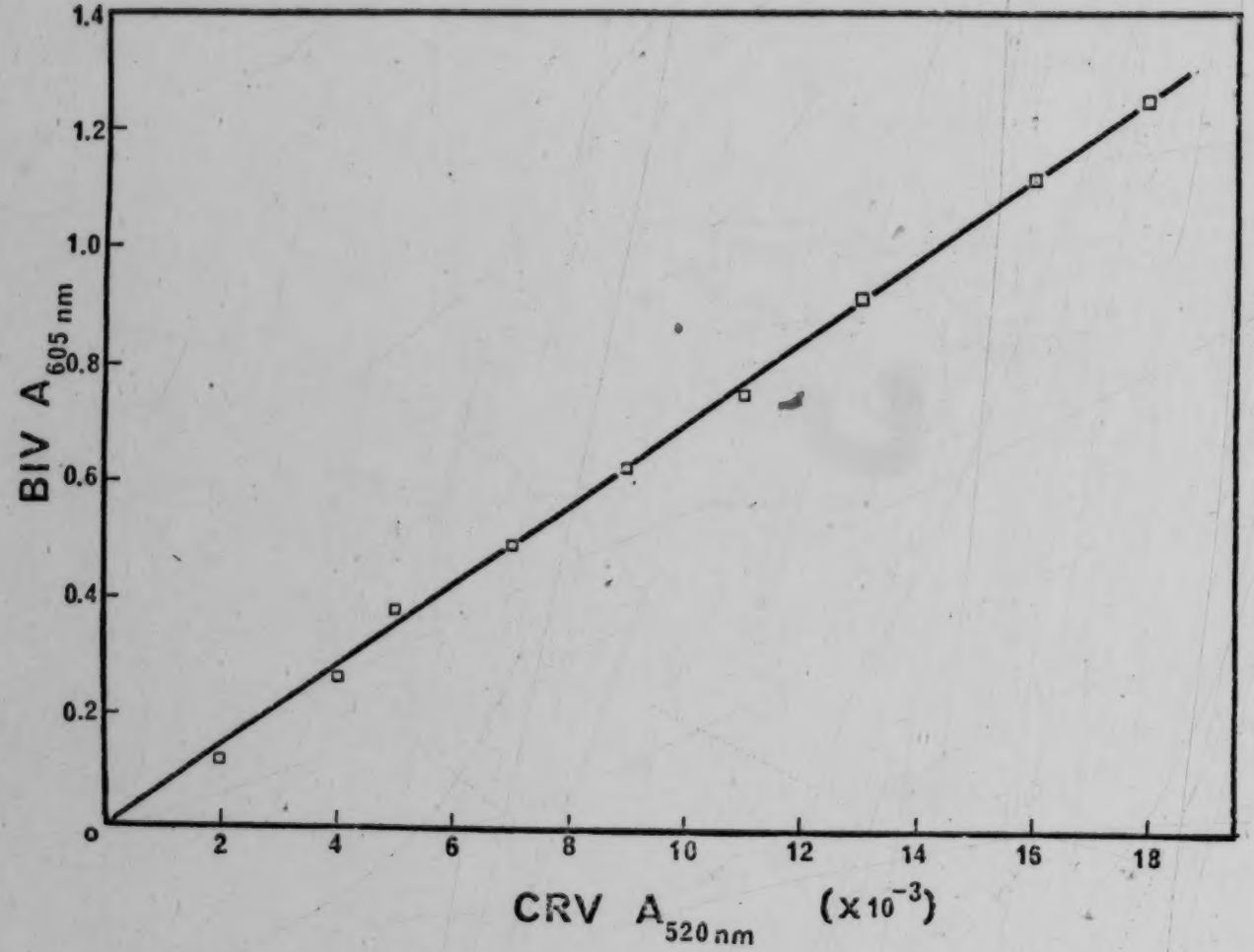


Figure 7. Correction curve for starch interference on the carbazole reaction.

4.3. MODEL STUDIES ON THE ROLE OF PME, CATIONS AND STARCH IN THE FIRMING EFFECT OF THE PRECOOK TREATMENT OF POTATO TISSUE.

A study with a model system consisting of purified potato cell wall and middle lamella (CW/ML), PME, starch and major potato tuber cations was undertaken to elucidate the role of these constituents in the firming of potato tissue during precooking.

4.3.1. Materials.

Southern Alberta Netted Gem potatoes, (25±1% dry matter): raw, and freeze-dried dices and powder of 150 mesh.

Freeze-dried, starch-free, preparations of CW/ML and hydrogen- (i.e., cation-free) cell wall and middle lamella (H-CW/ML).

Air-dried preparations of potato starch, H-starch and Ca-starch.

Citrus pectin, 55-60% degree of esterification (DE value), M.W.= 150,000-300,000. Nutritional Biochemicals Corp., Cleveland, OH.

Tomato pectin methylesterase, E.C. 3.1.1.11., lyophilized. Sigma Chemical Co., Louis, MO.

Amyloglucosidase. Pure Grade. Sigma Chemical Co.

Amylase. Pure Grade. Sigma Chemical Co.

Tham, Tris (Hydroxymethyl) Aminomethane. J.T. Baker Chemical Co., Phillipsburg, NJ.

Pipes, Piperazine-N, N'-bis[2-ethane sulfonic acid], pk_a = 6.8 at 25°C. Sigma Chemical Co., St. Louis, MO.

Std. 0.01M NaOH. Fisher Scientific Co., Fair Lawn, NJ.

C_2H_5OH, purified.

NH_4OH.

NaOH.

HCl.

H_2SO_4.

$CuSO_4$.

$Ca(CH_3OO)_2$.

$NaCH_3COO$.

CH_3COOH, glacial.

KCl.

$MgCl_2$.

$NaHSO_3$.

$Ca(OH)_2$.

$AgNO_3$.

α, D-Galacturonic acid, monohydrate.

α, D-Galactose.

All chemicals used were analytical grade, and are available from various suppliers. Deionized water was used unless otherwise specified.

4.6.2. Equipment.

Freeze-Dryer, Model FFD-42-WS. Virtis Research Equipment Co.

Buhler Tissue Disintegrator. Edward Buhler & Co.

Hobart Vegetable Slicer, Model H 4212. The Hobart Mfg. Co.

Virtis Homogenizer, Model 45. Virtis Co.

Metrohm Automatic Combi-titrator, Model 3D; includes pH Meter, Model E512; Impulsomat, Model E 473; Dosimat, Model E425. Metrohm-Herisau, AG., Herisau, CH - 9100, Switzerland.

Servall Centrifuge, Model SS4. Ivan Sorvall Inc., Norwalls, CT.

Constant temperature water-bath with a circulatory pump, Model Lo-temptrol 154. Precision Scientific Corp., Chicago, IL.

Temperature Gradient Incubator, Model Thermocon C-200, with

incubation tubes. Scientific Industries Inc. Mineola, NY.

Constant temperature baths at 60, 65, 70, and 100°C.

Ultraviolet Spectrophotometer, Model Unican SP 1800. Pye-Unicam Ltd., Cambridge, England.

Atomic Absorption Spectrophotometer, Model 153. Instrumentation Laboratory Inc., Lexington, MA.

Sintered glass funnels, 25-50 μm pore size. ACE Glassworks Inc., Vineland, NJ.

Texturometer, described in Section 4.2.2.2., fitted with a stainless steel probe with a menispherical end, 0.64 cm diameter, 3.94 cm length.

Cole Palmer recorder, Model 355. Cole Palmer International, Chicago, IL.

4.3.3. Procedures.

4.3.3.1. Sample Preparation.

Peeled raw potatoes were diced into 1 cm^3 cubes, washed of free starch, and freeze-dried following procedures described in section 4.2.4.3.1. Half of the dried sample was ground to 150-mesh with a Buhler tissue disintegrator, then stored at 4°C in screw-capped jars until used for preparation of enzyme extracts (Section 4.3.3.5.). The remainder was similarly stored until used for preparation of CW/ML.

4.3.3.2. Preparation of CW/ML and H-CW/ML.

The following procedure was developed to obtain a starch-free preparation of CW/ML. In a Virtis homogenizer at full speed, 25 g of the freeze dried raw potato dices were blended for 2 min with 100 ml of ice-cold water. The homogenate was transferred onto 4 layers of 100 mesh nylon screen. By squeezing intermittently, free starch was washed

away with water until the residue was free of starch when examined under a polarized-light microscope. The preparation was then freeze-dried, powdered to 35-mesh with a Buhler tissue disintegrator, and stored at 4°C in screw-capped jars until used for enzyme assay. The yield was 5.1±0.1% of the tuber weight. The preparation had 16.25% pectin as anhydrogalacturonic acid (AGA), 373±8 µmole free carboxylic acid (COO^-) groups per g CW/ML dry matter, and an average DE value of 55%.

H-CW/ML was prepared following the method of Keijbets et al. (1976). About 2.5 g freeze-dried CW/ML was rehydrated in 35% ethanol and all ions removed by successive 15 min treatments with three separate volumes of 75 ml 70% ethanolic 0.6M HCl. The preparation was then washed with 70% ethanol until the washings were free of chloride as shown by addition of a few drops of 1% $AgNO_3$. This was followed by successive 5 min dehydration steps with three separate 50 ml volumes of 96% and absolute ethanol, and diethyl-ether. Finally, the H-CW/ML preparation was dried at 25°C in Vacuo for 24 h, and stored in a screw-capped jar at 4°C.

4.3.3.3. Preparation of Starch, H-starch and Ca-starch.

Several washed and peeled potato tubers were immersed in ice-cold water containing 100 ppm Na_2SO_3, diced, and homogenized in a Waring blender with two volumes of ice-cold water. The slurry was squeezed through a 100 mesh polyster sieve cloth and the homogenate centrifuged at 2,500 x G for 10 min. The upper light brown layer of protein was removed from the sediment, and the lower layer of starch was resuspended in water and re-centrifuged. This procedure was repeated until no impurity was evident under the microscope. The starch yield was 55% of the tuber dry matter.

H-starch was prepared from potato starch by a procedure developed by Winkler (1960). An aliquot was analysed for moisture content by drying at 120°C until constant weight. Alkalimetric titration of such H-starch showed that the starch-bound phosphoric acid was 7006 µeq/100 g starch dry matter.

Ca-starch was prepared by slurrying H-starch in appropriate amounts of saturated $Ca(OH)_2$ to give preparations in which 25, 50, 75 or 100% of the primary phosphoric acid hydrogen (2335 µeq per 100 g starch dry matter) was neutralized. The reaction was considered to be complete when the pH equilibrated at 6. The slurry was then transferred onto a sintered glass funnel and filtered. Starch samples were dried at 25°C in vacuo, and stored in a desiccator over P_2O_5.

4.3.3.4. Mineral Composition.

Freeze-dried and ground samples (2.5g) were dry ashed in a Vycor dish. An initial 30 min charring at 200°C was followed by ashing at 500°C for 2 h. The sample was then cooled, wetted with a few drops of conc. HNO_3, and ashed for a further 1 h. The residue was then cooled in a desiccator and weighed. The mineral composition was determined after solubilization of the ash in 6M HCl under gentle boiling for 30 min. The solution was made up to volume and a diluted aliquot was analyzed in the presence of 0.1% $LaCl_3$ for Na, K, Ca and Mg by atomic absorption spectroscopy (AAS). The P content was determined spectrophotometrically at 830 nm as the heteropolymolybdo blue complex.

4.3.3.5. Enzyme Assay of PME, E.C. 3.1.1.11.

The method of Vas et al. (1967), based on a principle developed by Kertesz (1957), was followed for the determination of PME activity. An automatic titrator was used as a pH-stat meter. The rate of alkali

consumption while maintaining a predetermined pH value was considered a measure of enzyme activity.

The following preliminary studies were conducted to develop a method of extracting the enzyme and evaluating its activity.

4.3.3.5.1. Enzyme extraction procedure.

Since PME is present in a bound form, aqueous NaCl was used as an ionic medium to desorb it from the water-insoluble cell particles. The effect of NaCl concentration and the volume of the extracting fluid on the amount of enzyme extracted were studied.

NaCl solutions of 0, 3, 5, 7 and 10% (w/v) were used. Raw potato dices (20 g), previously dried with paper towels, and 50 ml of NaCl solution were thoroughly blended at full speed for 2 min in a Virtis homogenizer. The slurry was left at 25°C for 30 min to allow complete extraction, and then filtered through 8 layers of cheese cloth. The filtrate was centrifuged at 12,000 x G for 20 min with Servall centrifuge The supernatant, designated as the enzyme extract, was used to determine the PME activity. When necessary, the extract was stored at 4°C for up to 5 days, during which period no change in activity was observed.

The following ratios of the extraction fluid (NaCl) and potato were chosen to determine the maximal extraction: 1.0:1, 1.5:1, 2.0:1, 2.5:1, and 3.0:1. The weight of potato and volume of aqueous NaCl used were such that each solution weighed 40 g. The NaCl concentration was 4.5% in all the preparations.

It was found that the best extraction was obtained when the ratio of fresh potato to extraction fluid (1M NaCl) was 1:2 (w/v). This extraction procedure was, therefore, used for all further work.

4.3.3.5.2. Evaluation of the method for PME activity determination.

It was desirable to find the most suitable experimental conditions for determination of PME activity. Therefore, the effects of substrate, enzyme, and NaCl concentration were examined at pH 7.5 and 30°C.

The effect of substrate concentration was studied by varying the pectin concentration from 0 to 0.6% in 0.06% intervals. The reaction mixture contained 5 ml pectin solution of a given concentration and 1 ml of enzyme extract.

The effect of enzyme concentration on its activity was monitored by varying the amount of enzyme extract from 0 to 3.0 ml in 0.5 ml intervals. Appropriate volumes of 0.6% pectin solution were added to maintain the volume of the reaction mixture at 6 ml. Heat deactivated enzyme served as a control.

The effect of NaCl concentration on PME activity was determined at the following levels: 0.7 to 3.0% intervals, and 4, 5 and 6%. Solid NaCl was added, if necessary, to achieve high NaCl concentrations.

4.3.3.5.3. pH and temperature Optima for PME activity.

The most satisfactory combination was 2 ml enzyme extract and 4 ml 0.6% pectin solution. The optimum pH for PME activity at 30°C was established by varying the pH of the reaction mixture between 5.0 and 9.0. Heat deactivated PME served as a control to detect spontaneous desterification of the pectin at higher pH values.

The optimal temperature for PME activity was established by holding the reaction mixture at its optimal pH and increasing the temperatures from 30°C to 75°C.

4.3.3.5.4. PME activity in freeze-dried potato and CW/ML.

Six tubers of uniform size (500±30 g) were lightly peeled, diced

into 1 cm^3 cubes, and thoroughly mixed to obtain a composite sample. Triplicate samples of 20 g each were taken for moisture analysis.

Triplicate samples of 40 g raw potatoes were taken for enzyme extraction with 80 ml of 1M NaCl, following the procedure described previously. The enzyme activity was assayed at pH 7.5 and 30°C using 4 ml of 0.6% pectin solution and 2 ml of the enzyme extract.

The remainder of the potato cubes were freeze-dried and powdered to 150-mesh. Duplicate samples of 10 g potato (or 600 mg CW/ML), both approximately equivalent to 40 g raw potato, were extracted with 80 ml 1M NaCl in the usual manner, and the enzyme activity was assayed as before. PME activity was expressed as μmole carboxyl groups released per g of dry matter in potato.

4.3.3.5.5. Effect of SO_2 on PME activity.

Samples of 40 g diced raw potato were immersed separately in 80 ml of 1M NaCl containing Na_2SO_3 such that the SO_2 concentration in the 120 g mixture was 0, 50, 300, 500 and 1000 ppm. After 15 min, the mixture was homogenized to obtain the PME extract and the enzyme activity was assayed in the usual manner.

4.3.3.6. Effect of Precooking Temperature on the DE and the Solubilization of Pectins in the CW/ML.

4.3.3.6.1. Temperature gradient incubation.

Duplicate samples of 50 mg of freeze-dried CW/ML preparation in 10 ml of 0.02M Pipes-Tris buffer, pH 6.1, were incubated for 30 min in 15 ml incubation tubes using a temperature gradient incubator at 25, 50, 55, 60, 65, 70, 75 and 100°C.

After immersing the tubes in ice-cold water, the contents were transferred onto a sintered-glass funnel, and filtered with suction.

The filtrate was collected and stored until analyzed for uronide and galactose contents.

4.3.3.6.2. Cu^{2+} ion exchange technique for determination of DE values and pectin content.

The residue, still on the filter, was analyzed for pectin content and DE value essentially following the procedure of Keijbets and Pilnik (1974a). Any CW/ML material remaining on the tube walls was first rinsed onto the filter with 70% ethanol. It was then washed with two 10 ml aliquots each of 70%, then 35% ethanol. The residue was mixed with three separate 25 ml aliquots of 1% $CuSO_4$ solution, pH 3.5. Each aliquot of $CuSO_4$ was allowed to gradually percolate through for 15 min prior to the use of suction.

The physically adsorbed Cu^{2+} ions were washed away repeatedly with water until the filtrate showed a negative reaction for Cu^{2+} with conc. NH_4OH. The residue was then washed with three 25 ml aliquots each of 35% followed by 70% ethanol to avoid lumping. About 5 min contact time were allowed with each washing before the use of suction.

The chemically bound Cu^{2+} ions were exchanged for H^+ ions with 0.6M HCl in 70% ethanol using three separate 10 ml aliquots and a 5 min contact period between elutions. The desorbed Cu^{2+} ion solution was made up to 50 ml with 70% ethanol, and stored at 4°C until analyzed for Cu^{2+} content by atomic absorption spectrophotometry (AAS).

The residue was then saponified with a sufficient quantity of 0.1M NaOH in 60% ethanol for 1 h as the alcoholic alkali seaped through the filter. It was then washed for 15 min with 60 ml of 1M acetic acid in 70% ethanol then several times with 70% ethanol. The ion-exchange procedure with Cu^{2+} was then repeated, and the filtrates containing the

exchanged Cu^{2+} ions collected for analysis of copper.

4.3.3.6.3. Determination of copper content by AAS.

Ten ml aliquots of the filtrates were placed in a vacuum oven at 60°C for 5 h to evaporate the ethanol, then diluted with appropriate amounts of water. The Cu^{2+} content was analyzed with AAS using a standard curve. The instrumental parameters are shown in the Appendix. The amounts of Cu^{2+} chemically bound before and after saponification were used to calculate the DE values and pectin content of the CW/ML. (see Appendix).

4.3.3.6.4. The carbazole reaction method for uronide analysis.

The Rouse and Atkins' carbazole reaction test, as modified by McComb and McCready (1952) and Potter and McComb (1957), was used for determining the uronide content of the filtrates. This was followed by the phenol-sulphuric acid test (Dubois et al., 1956) to determine the galactose content (Figure 9). The uronide content of the filtrate was then obtained from a standard curve (Figure 6), corrected for galactose interference using a correction curve (Figure 8), and expressed as mg AGA per 100 mg dry CW/ML preparation.

4.3.3.7. Pectin Changes in CW/ML Induced by Potato Constituents During the Precook Treatment.

The effect of Ca^{2+} and Mg^{2+} availability, starch, PME and the precooking temperature during boiling of CW/ML, with and without prior precook treatment, on pectin solubilization was investigated. The significance of cooling between precooking and final cooking was also studied.

4.3.3.7.1. Effect of Ca^{2+}, PME and temperature during precooking.

Precooking involved incubation of 25 mg H-CW/ML and 5.0 ml 0.02M

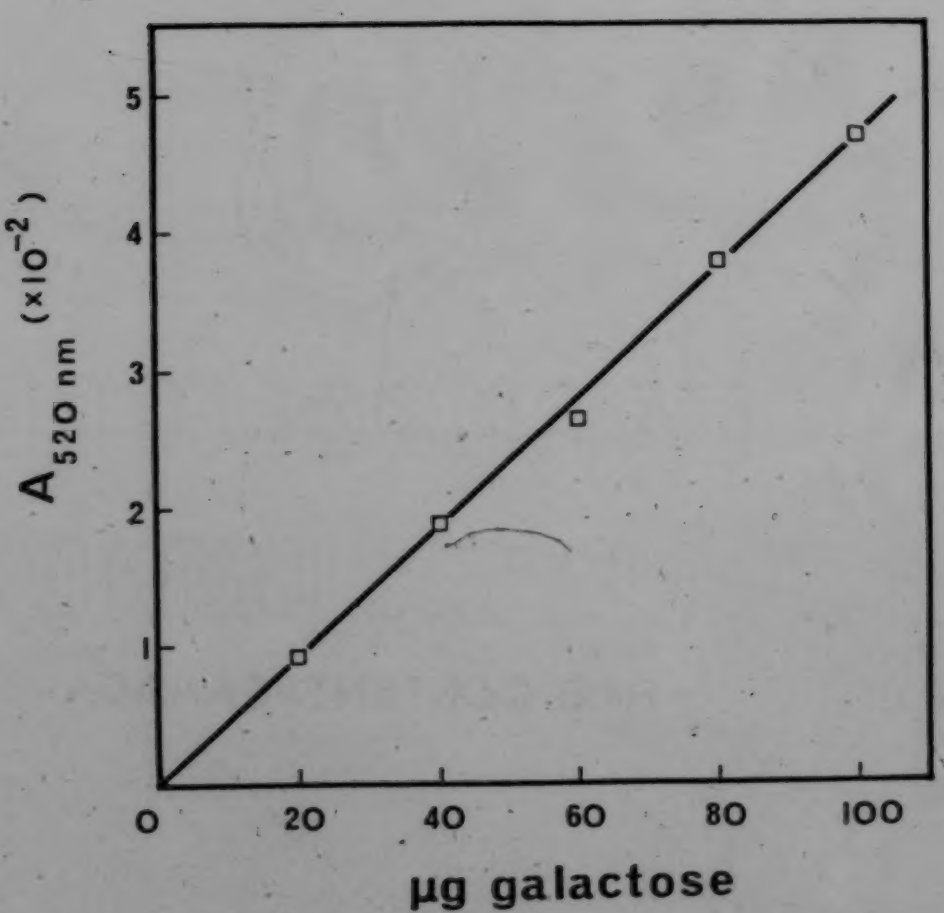


Figure 8. Correction curve for the galactose interference on the carbazole reaction.

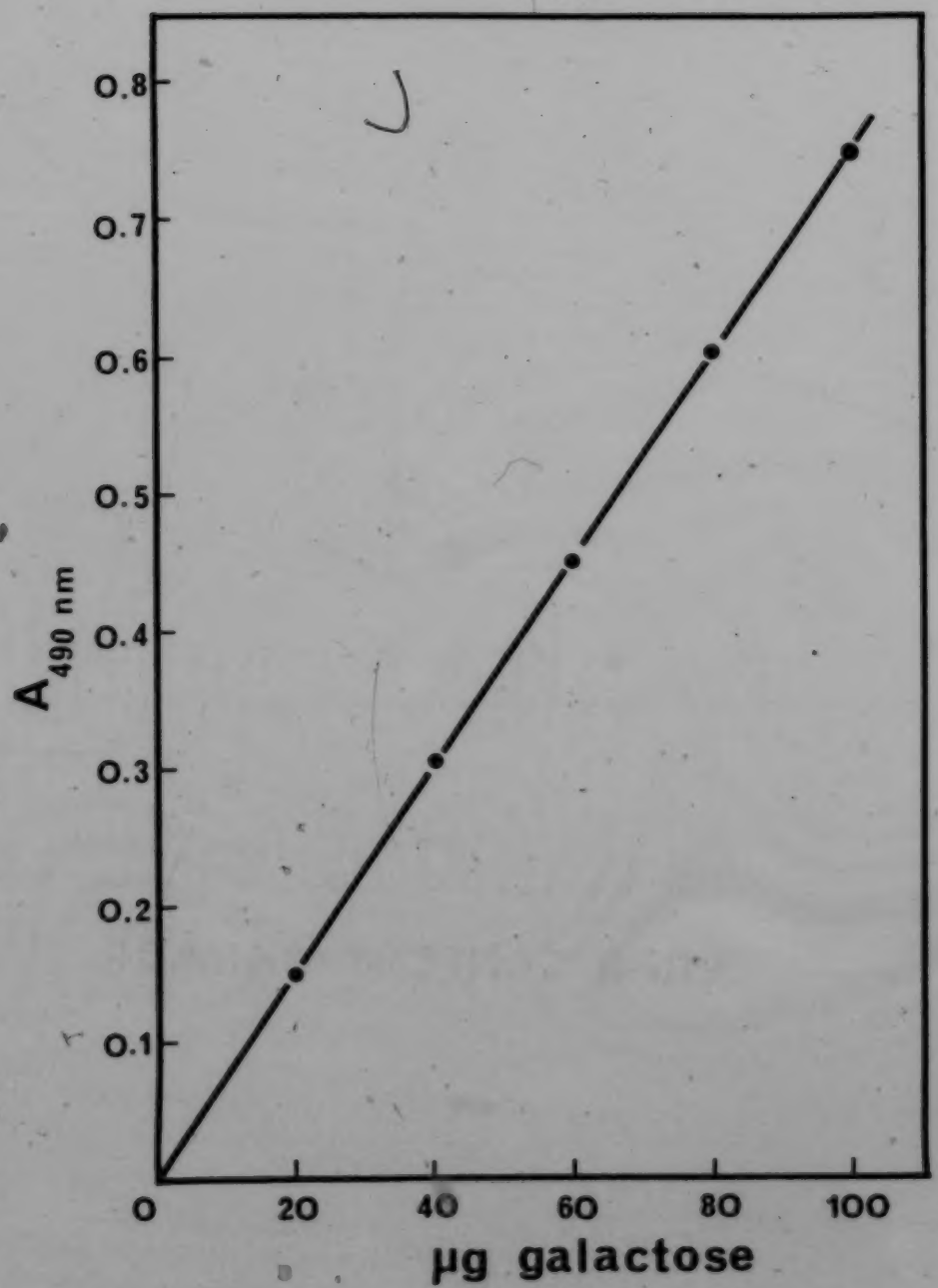


Figure 9. Standard curve for galactose determination by the phenol-sulphuric acid method.

Pipes-Tris buffer, pH 6.1, in capped culture-tubes for 30 min at 60, 65 and 100°C.

To study the influence of Ca^{2+} availability, appropriate amounts (in µl quantities so as to minimize volume changes) of 0.3M CaCl were added to four separate tubes of the above mixtures to give ratios of added Ca^{2+} to non-esterified carboxyl groups of the CW/ML pectic galacturonan (Ca^{2+}/COO^{-}) of 0, 0.5, 1.0 and 5.0.

The effect of PME was studied by replacing part (0.5 ml) of the buffer with 0.5 ml of tomato PME such that the enzyme activity in the incubation mixture was comparable to that of the potato enzyme extracts. The solution was prepared by dissolving tomato PME in 10% NaCl to give an activity of 14.4 enzyme units per ml.

The mixtures were incubated for 30 min, with frequent agitation to ensure proper mixing, then immediately placed in ice water to terminate the reaction. The contents were then transferred onto sintered-glass funnels. The filtrates were analyzed for solubilized uronide and galactose contents.

The CW/ML residue was transferred from the tube onto the same funnel with the aid 70% ethanol, and the physically adsorbed Ca^{2+} was removed with repeated washing with 70% ethanol. The chemically bound Ca^{2+} was eluted by mixing the residue on the sintered-glass funnel for 5 min each with two 10 ml aliquots of 0.6M HCl in 70% ethanol. The calcium eluate, made up to 25 ml with 70% ethanol, was suitably diluted following a procedure similar to that for Cu^{2+} (section 4.3.3.6.3.) and then analyzed for Ca^{2+} content using AAS.

4.3.3.7.2. Effect of Ca-starch as a Ca^{2+} source during precooking.

Precooking consisted of incubating 20 mg H-CW/ML 350 mg H-starch

and 5.0 ml 0.02M Pipes-Tris buffer of pH 6.1 at 60, 70 and 100°C for 30 min in capped culture-tubes. To study the effect of Ca^{2+} availability, four separate mixtures were prepared with Ca-starch having 25, 50, 75, and 100% of the phosphate groups neutralized.

The following procedure was adopted to remove the gelatinized starch before pectin analysis: After the incubation was terminated by immersing the tubes in ice-cold water, the contents were frozen at -10°C for 30 min, then at -29°C for 30 min. Acetate buffer, 3.5 ml, pH 4.8, 0.1M, was added to the thawed mass, and the mixture was centrifuged at 14,000 x G for 10 min to obtain the supernatant.

A 0.5 ml solution of amyloglucosidase, having an enzyme activity of 25 E.U., was added to a 5.0 ml aliquot of the above supernatant, and the mixture was incubated at 50°C for 1 h. This treatment was found to be adequate for complete hydrolysis of the starch (as indicated by a spot test using 1 drop of the above mixture and 1 drop of 0.004 N iodine solution). Amyloglucosidase was prepared by dissolving a pure protein preparation, having an activity of 10 E.U. per mg, at a level of 5.0 mg per ml in 0.1M acetate buffer of pH 4.8.

When the contents had cooled to 35°C, 0.5 ml of glucose oxidase, containing 8 mg protein per ml in a pH 4.8 acetate buffer, was added and the mixture was incubated at 35°C for 1 h under aeration with compressed air. The reaction was terminated by boiling for 5 min. After cooling to room temperature, the original volume was restored with water, and the tubes centrifuged at 12,500 x G for 10 min. The supernatant was collected and analyzed for uronide and galactose contents as before. The blank sample was prepared following all the above steps, except H-CW/ML and starch were omitted.

4.3.3.7.3. Effect of Ca^{2+} and Mg^{2+} during precooking, cooling and final cooking.

The experimental procedure was the same as that in section 4.3.3.7.2. The treatment consisted of precooking at 65°C for 30 min in presence and in absence of PME, and cooking at 100°C for 30 min with and without an intermediate cooling step (25°C for 20 min). The above test samples contained 50% Ca-starch as a source of Ca^{2+}.

To study the influence of Mg^{2+}, an appropriate amount of 0.3M $MgCl_2$ was added to a buffered H-CW/ML preparation such that the ratio of added Mg^{2+} and non-esterified carboxyl groups of the CW/ML pectic galacturonan (Mg^{2+}/COO^-) was 1.0. Buffered H-CW/ML and H-starch served as a control, and pure buffer as the blank.

4.3.3.8. Effect of Calcium on Tissue Firming During the Precook Treatment.

4.3.3.8.1. Treatments.

Several peeled and washed tubers of uniform size (300±25 g) were cut into 1.27 cm thick slices and immersed in water containing 100 ppm Na_2SO_3. The slices were precooked at 65, 70 or 75°C for 30 min in four parts by weight of water, with or without 200 ppm Ca^{2+} (as Ca-acetate). Then the slices were cooled to 25°C for 20 min in four parts by weight of water, again with or without the Ca^{2+}. The precooked and cooled slices were then either steam-cooked or boiled in water, with or without Ca^{2+}. In some treatments the precooking and/or cooling steps were omitted. All the treatments are listed below:

1. Cooked in water.
2. Cooked in 200 ppm Ca^{2+}.
3. Precooked (65°C), cooled, and cooked in water.

4. Precooked (75°C), cooled, and cooked in water.

5. Precooked (75°C), cooled, and cooked in water.

6. Precooked (70°C), and cooked in water.

7. Precooked (65°C), cooled, and cooked in 200 ppm Ca^{2+}.

8. Precooked (70°C), cooled, and cooked in 200 ppm Ca^{2+}.

9. Precooked (75°C), cooled, and cooked in 200 ppm Ca^{2+}.

10. Precooked (70°C) in 200 ppm Ca^{2+}, cooled in 200 ppm Ca^{2+}, and cooked in water.

11. Precooked (70°C) in 200 ppm Ca^{2+}, cooled in water, and cooked in 200 ppm Ca^{2+}.

12. Precooked (70°C), and cooked in 200 ppm Ca^{2+}.

13. Precooked (70°C), and cooled in water, and steam-cooked.

14. Precooked (70°C) in water, and steam-cooked.

15. Precooked (70°C), and cooled in 200 ppm Ca^{2+}, and steam-cooked.

16. Precooked (70°C) in 200 ppm Ca^{2+}, and steam-cooked.

17. Steam-cooked.

4.3.3.8.2. Texture Measurement.

The slices were cooled to 25°C, and a random selection was made for penetration force measurement. The texturometer described in section 4.2.2.2. was used, except that the plunger was replaced with a stainless steel hemispherical-end probe, 0.64 cm in diameter and 3.94 cm in length. The penetration force was measured by driving the probe vertically onto the slice until it had penetrated 1 cm. The force was recorded, and the maximum height of the peaks, calibrated in terms of g-force, was designated as the penetration force and considered to be a measurement of tissue firmness.

4.4. FURTHER DEVELOPMENT OF THE F-T PROCESS

The study was undertaken primarily to make modifications of the present batch-scale pilot plant so as to enable semi-continuous operation of the freeze-thaw process for the production of potato granules.

Detailed studies of the processing parameters were also conducted under batch operation to obtain optimum processing conditions with respect to:

1. The temperature of the thawed mash for efficient predrying.
2. The moisture content of the predried product for efficient granulation.
3. Variation of raw material.
4. Efficient stirrer design.

Under a semi-continuous operation, the processing parameters studied were air velocity, temperature and time optima for predrying, granulation and final drying.

4.4.1. Materials.

Southern Alberta Netted Gem potatoes, 25±1% dry matter.

Northern Alberta Netted Gem potatoes, 19±1% dry matter.

Southern Alberta Norgold potatoes, 22±1% dry matter.

Surfactant Myvatex, Type 3-50. Eastman Kodak Co., Rochester, NY.

Na_2SO_3. Fisher Scientific Co. Fair Lawn, NJ.

4.4.2. Equipment.

Hobart vegetable slicer, Model H4212. The Hobart Mfg. Co., Troy, OH.

KitchenAid Mixer equipped with a flat beater. The Hobart Mfg. Co.

Atmospheric steam cooker with a cover lid.

Stainless steel trays.

Air-blast freezer with minimum air temperature of -29°C and air velocity of 1.42 $m^3 s^{-1}$.

Manesty Petrie Fluid bed Dryer, Model MP.10.E., as modified by Ooraikul (1973). Manesty Machines Ltd., Speke, Liverpool, England.

Speedomax 12-point temperature recorder. Leeds and Northrup (Canada) Ltd.

The Cyclone Collection System including the 2 HP, 3600 rpm open drip-proof motor of the Bowen Conical Laboratory Spray Dryer. Bowen Engineering, Inc., North Branch, NJ.

"Veeder" Speedometer. The Veeder Mfg. Co., Hartford, CT.

Canadian Standard Sieve Series, and portable sieve shaker. The W.S. Tyler Co. (Canada) Ltd., St. Catherine, Ont.

4.4.3. Procedures.

4.4.3.1. Effect of Product Temperature at Predrying.

2.5 kg batches of Netted Gem potatoes (25±1% dry matter) were processed into granules. Every batch followed the same processing procedure except that the frozen mash was thawed to a varying degree and tempered so that the potatoes entering the predrying step had temperatures ranging from about 0-12°C.

The final product was sifted for 15 min with a series of standard sieves, and the amount of discard (particles >18 mesh) and the yield (fine granules of <60 mesh) were determined as a w/w% of the total dried product. The number of broken cells was assessed as before.

4.4.3.2. Effect of Moisture Content at Granulation.

2.5 kg batches of Netted Gem potatoes with an initial moisture content of 75±1% were processed following the parameters previously determined to be optimal. Every batch followed the same processing

procedure except that the predrying step was either lengthened or shortened so that the potatoes entering the granulation step had moistures ranging from about 30 to 50%.

Moisture was determined by heating the predried sample in an oven under a vacuum of 76 mm Hg at 70°C for 48 h. The percent yield, discard and broken cells were determined as previously described.

4.4.3.3. Variation of Raw Material.

2.5 kg batches of potatoes having different dry matter content were processed into granules with the batch F-T technique. The potatoes used were Netted Gems of approximately 25 and 19%, and Norgolds of 21% solids. Processing parameters such as stirrer speed, inlet air-temperature, and velocity were altered as needed at each step to ensure successful operation.

4.4.3.4. Process Parameters and Stirrer Design.

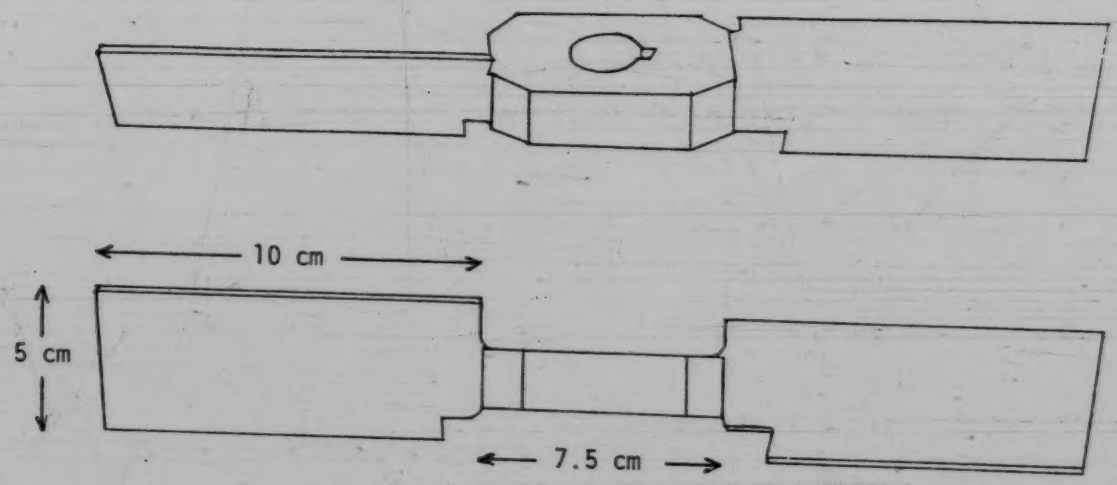
During the predrying stage, a "turning and mixing" of the mash is desirable. A stirrer was designed to optimize this effect (Figure 10). For efficient granulation, a controlled degree of attrition forces is desirable, therefore, another stirrer was designed to optimize "impact" and "shear" forces, the two major attrition forces involved in granulation by the F-T process (Figure 11).

Using these two different stirrers at the predrying and granulation stages, processing parameters, primarily stirring speed, temperature and velocity of the inlet air were manipulated to achieve the most efficient predrying and granulation.

4.4.3.5. Semi-continuous Operation of the F-T Process.

The Manesty Petrie fluid bed dryer modified by Ooraikul (1973) was further modified by connecting it to the cyclone collection system of the

Figure 10. Stirrer designed for efficient predrying.



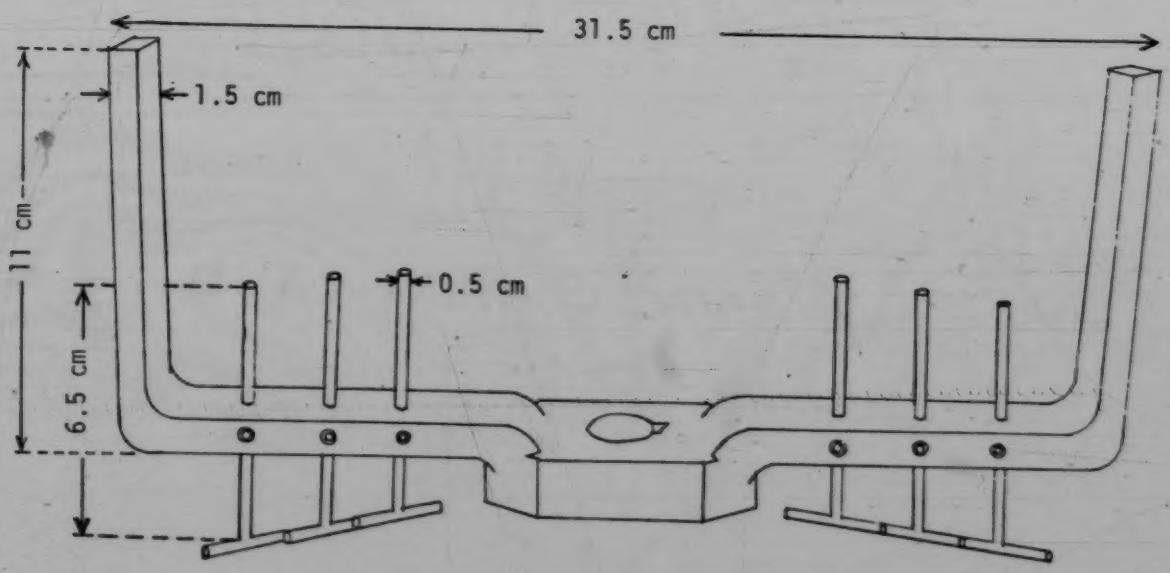


Figure 11. Stirrer designed for efficient granulation.

Bowen Conical Laboratory Spray Dryer. The fan motor of the fluid bed dryer was removed and replaced with the cyclone separator and the motor of the spray dryer by means of a stainless steel pipe system having a 15.5 cm internal diameter. The fluidizing bowl and the pipe systems were connected with canvas cloth and metal rings to ensure air flow through the fluid bed. The general set up of the equipment is illustrated in Figures 12 and 13.

The air flow through the system was controlled by means of butterfly valves attached to the air inlet and exhaust pipes. The air velocity was monitored with a manometer system designed and described by Ooraikul (1973). Wet bulb and dry bulb thermocouples were placed at suitable positions in the air inlet pipe to measure the wet- and dry-bulb temperatures of the incoming air. Two other thermocouples were suitably positioned to measure the temperatures of the drying and the exhaust air. The stirrer speed was determined using the "Veeder" speedometer.

The moisture content of the predried and the final product, the percent yield, discard and broken cells were determined as described previously.

For the operation of the semi-continuous unit, 2.0 kg of frozen and thawed mashed potatoes were charged into the fluid bowl and processed into granules following the steps outlined by Ooraikul (1973, 1977).

During predrying, the processing parameters were set such that within a 20 min period the fluidized particles were dried to a moisture content within the critical level of 40-45% and were progressively transferred to the cyclone collector. At the end of

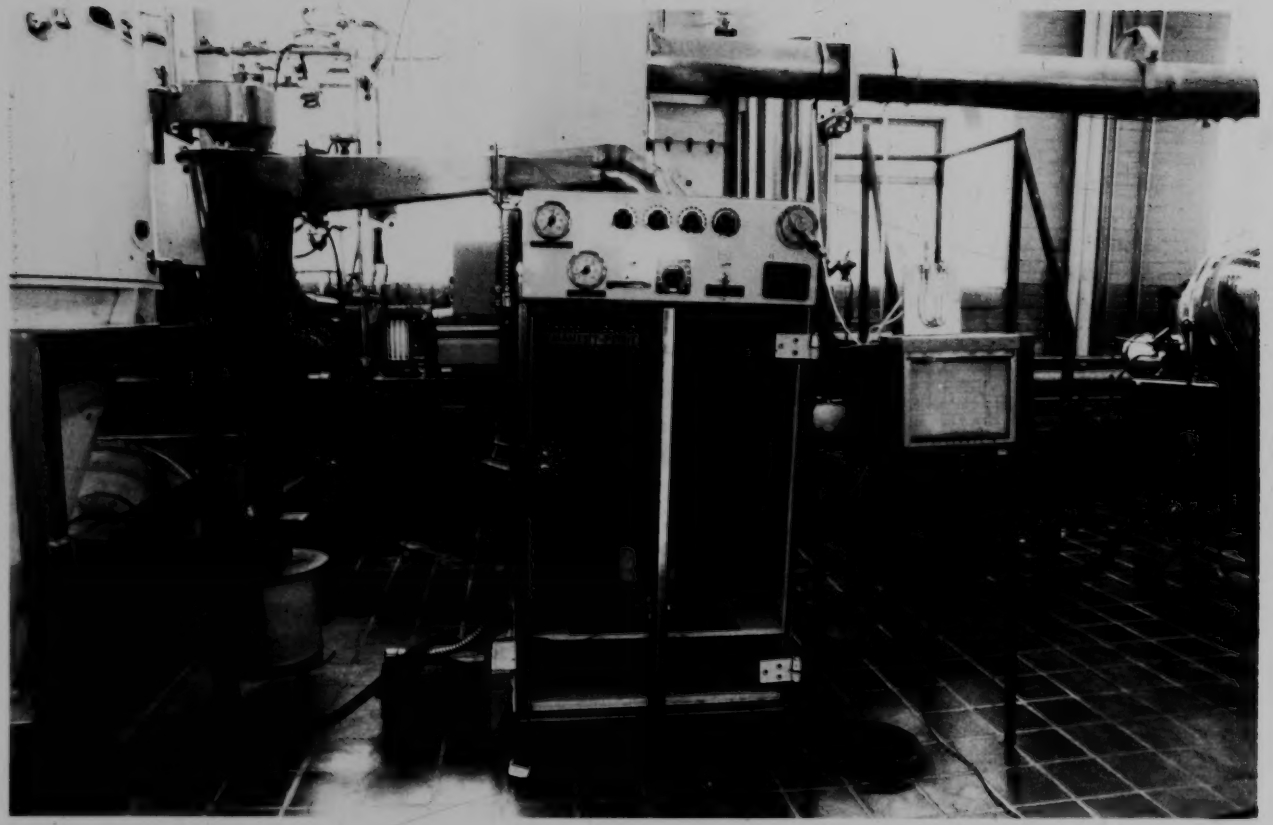
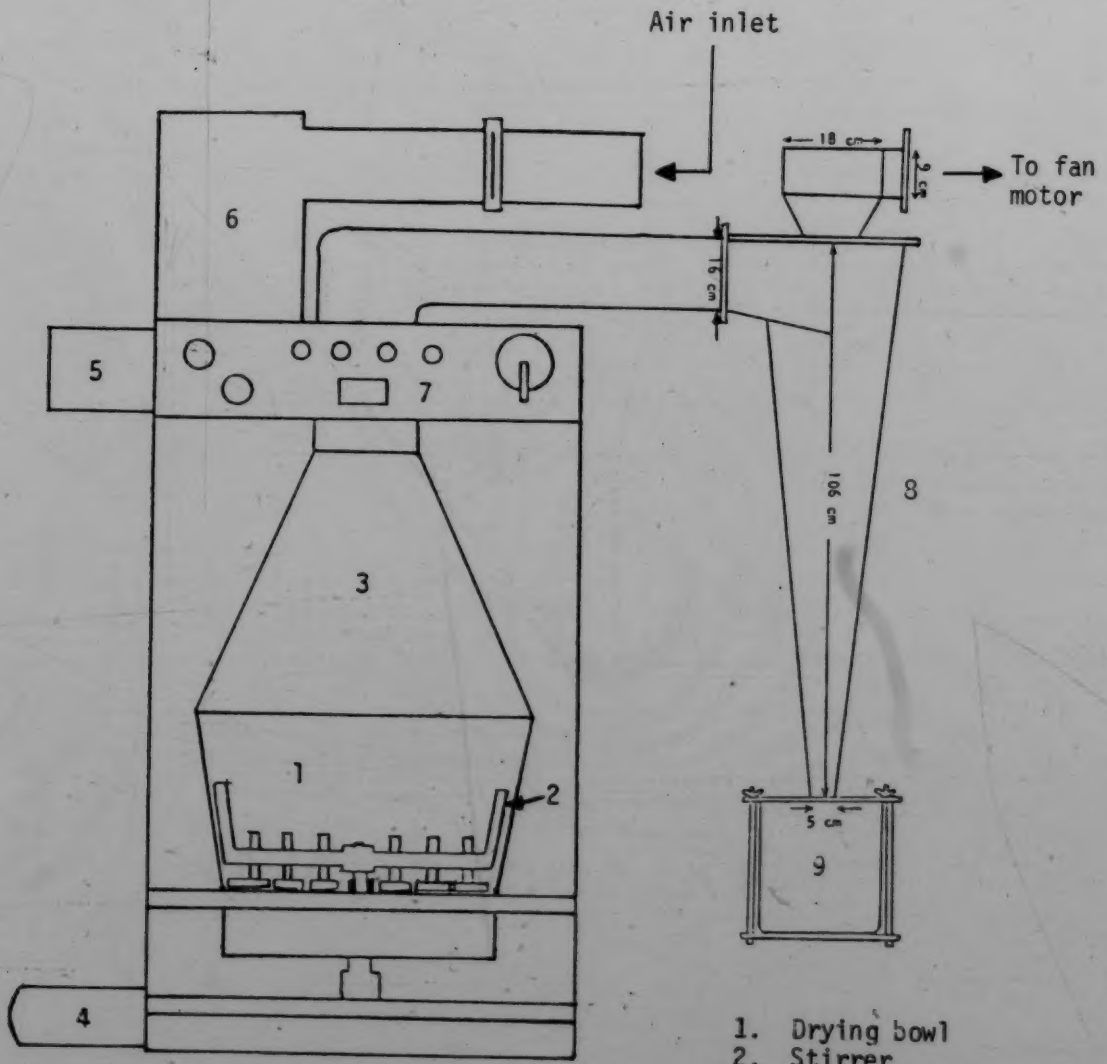


Figure 12. The fluid bed dryer and cyclone collection system used for the semi-continuous operation of the F-T process.

Figure 13. Illustration of the general set up of the equipment for the semi-continuous operation of the F-T process.



FLUID BED DRYER

1. Drying bowl
2. Stirrer
3. Canvas connector
4. Stirrer motor
5. Speed controller
6. Heater
7. Control panel
8. Cyclone separator
9. Collection jar

predrying only large particles, consisting of unmashed pieces and large aggregates of several cells, remained in the fluid bowl.

For granulation, the predried product, consisting mainly of agglomerates of several cells, was recharged into the fluid bowl fitted with the stirrer designed for granulation. In this step no heat was applied to the incoming air, and the stirrer speed was increased to generate the minimal force required to separate the predried agglomerates into single whole cells. The air velocity was such that granulated cells would be entrained and progressively removed from the fluid bed within the 10 min granulation period.

The granulated product was finally dried at a suitable air temperature and velocity such that, as the fluidized particles were dried to a desired moisture content (about 7%), they were entrained in the air stream and were transferred to the cyclone collector.

4.5 PHYSICOCHEMICAL CHANGES DURING AGING OF POTATO GRANULES.

This study was undertaken to understand the physicochemical changes occurring during the aging process of potato granules, and to relate these changes to the rehydration rate of the granules and the extrusion properties of the dough for the production of extruded French fries. The following properties were characterized for both the Add-Back and the Freeze-Thaw granules:

1. Water holding capacity (WHC).
2. Swelling power, cold water swell (CWS).
3. Degree of retrogradation.
4. Percent moisture content.
5. Reconstitution time.
6. Extrusion properties.

4.5.1. Materials and Equipment.

Add-back and Freeze-thaw granules aged for different periods of time.

15 ml and 50 ml tapered and graduated centrifuge tubes.

International Centrifuge, Model X-2, with 25 ml and 50 ml swinging bucket heads. International Equipment Co. Ltd., Boston, MA.

Wrist-Action Shaker. Burrell Corp., Pittsburgh, PA.

Constant-temperature chamber. Labline Inc., Chicago, Il.

Buhler Tissue Disintegrator. Edward Buhler & Co.,Tubingen, W. Germany.

Spectronic 20 Spectrophotometer. Bausch and Lomb Inc., Rochester, NY.

Iodine, resublimed. Fisher Scientific Co. Fair Lawn, NJ.

KI, granular. Fisher Scientific Co.

Pototo starch. Sigma Chemical Co., St. Louis, MO.

Water-bath at 70°C.

Magnetic stirrer. Corning Co., Corning, NY.

Magnetic stirring rod, 1 x 7.5 cm.

F.I.R.A./N.I.R.D. Extruder. H.A. Gaydon & Co. Ltd., Croydon, England.

4.5.2. Procedures.

4.5.2.1. Water Holding Capacity (WHC).

The method of Medcalf and Giles (1965), with the modifications suggested by Morrow and Lorenz (1974) for determining bound water for cereals, was applied to determine % WHC of potato granules. A sample of 0.50 g was added to 10 ml distilled water in a tared 15 ml tapered centrifuge tube. The tubes were stoppered and agitated for 1 h at a rate of 1 cycle/sec with a wrist-action shaker placed in a constant temperature (25.0±0.1°C) chamber, and then centrifuged for 30 min at 2,000 x G. The supernatant was carefully decanted and excess water wiped dry with a tissue. The tubes were then weighed to determine % WHC, expressed as weight of water retained per 100 g dry matter. The results reported were the average of four determinations.

4.5.2.2. Swelling Power, Cold Water Swell (CWS).

The method described by Potter (1954), with minor modications, was used to determine CWS. Potato granules, 2.50 g, were placed in a 50 ml graduated centrifuge tube and mixed with sufficient water at 25°C to make 25 ml of a homogeneous slurry. The tubes were stoppered and their contents mixed for 1 h at an agitation rate of 1 cycle/sec with a wrist-action shaker placed in a constant temperature (25.0±0.1°C) chamber. When the mixing was complete, the tubes were removed and centrifuged for 15 min at 1,000 x G. The supernatant was swiftly decanted, 10 ml of distilled water were carefully pipetted into the tube, and the total volume determined. The volume of the swollem material, designated as CWS, is equal to the total volume minus 10

times 4. The values reported, expressed on the basis of 10 g total solids, were the average of four determinations.

4.5.2.3. Degree of Retrogradation.

Two grams of sample and 25 ml distilled water were thoroughly blended for 30 min with a tissue disintegrator containing about 25 g glass beads. The apparatus was kept cool with a water jacket at 18±1°C. The homogenate was quantitatively transferred into a 250 ml volumetric flash using distilled water, made up to the mark, and then magnetically stirred at room temperature for 1 h. About 40 ml of the extract was centrifuged for 30 min at 2,500 x G. The supernatant was carefully decanted and diluted if necessary. Whenever diluted, the supernatant was placed in a 70°C water-bath, cooled to room temperature, and distilled water added to make up for any evaporative losses. This was to ensure that any starch precipitated due to the "dilution-effect" was redissolved.

Suitably diluted aliquots of 2.5 ml were taken for determination of soluble starch content as described by Ooraikul et al. (1974), (See Figure 5 also). Soluble starch was expressed as absorbance units per g dry matter. The results reported were the average of four determinations.

4.5.2.4. Percent Moisture Content (% M.C.).

Approximately 10 g of the granules, accurately weighed, were dried until constant weight was reached (48 h) in a vacuum oven (76 mm Hg) at 70°C. % M.C. was expressed on a wet basis. All samples were vacuum packaged in water-impermeable pouches and stored at room temperature.

4.5.2.5. Reconstitution Time.

This method is a simulation of the reconstitution procedure used in the institutional production of extruded French fries (Tamura and Packer, 1976). Potato granules, 30.0 g, were fed through an 8.5 cm glass funnel, the opening of which was adjusted by means of a flexible tube and a clamp such that all the granules passed through in 12 sec, into a beaker of 9.0 cm diameter containing 63 ml of tap water at 18±1°C. The contents of the beaker were mixed vigorously with a 1 x 7.5 cm magnetic stirring rod set at a constant speed setting of 4.5. The time taken from the first contact of the granules and the water until the magnet stopped moving due to the "setting" of the slurry into a firm dough represented the reconstitution time in sec.

4.5.2.6. Extrusion Properties.

A granule sample of 50.0 g was reconstituted with tap water (18±1°C) at a ratio of 1:2 (w/v) of granules: water, allowed to "set" and "condition" for 30 min at room temperature in a covered container. The dough was carefully and uniformly packed into the load cell ensuring that no air was occluded, and the force required to extrude the sample, designated as "extruder thrust", was determined using the F.I.R.A./N.I.R.D. Extruder at a gear speed of 4. Values reported were an average of four determinations.

The basic principle of the F.I.R.A./N.I.R.D. Extruder is that a sample tightly packed in a cylindrical load cell is forced from this cell through a 3.18 mm diameter orifice by a plunger made of a solid cylindrical rod of a diameter which just allows free movement through the load cell. The plunger moves at a uniform speed of 7.62 cm/sec. The thrust required to extrude the sample is recorded on a moving chart

throughout the extrusion test, and this chart serves as a record of the extrusion and various other rheological properties of the sample. A typical thrust vs extrusion curve is shown in Figure 14.

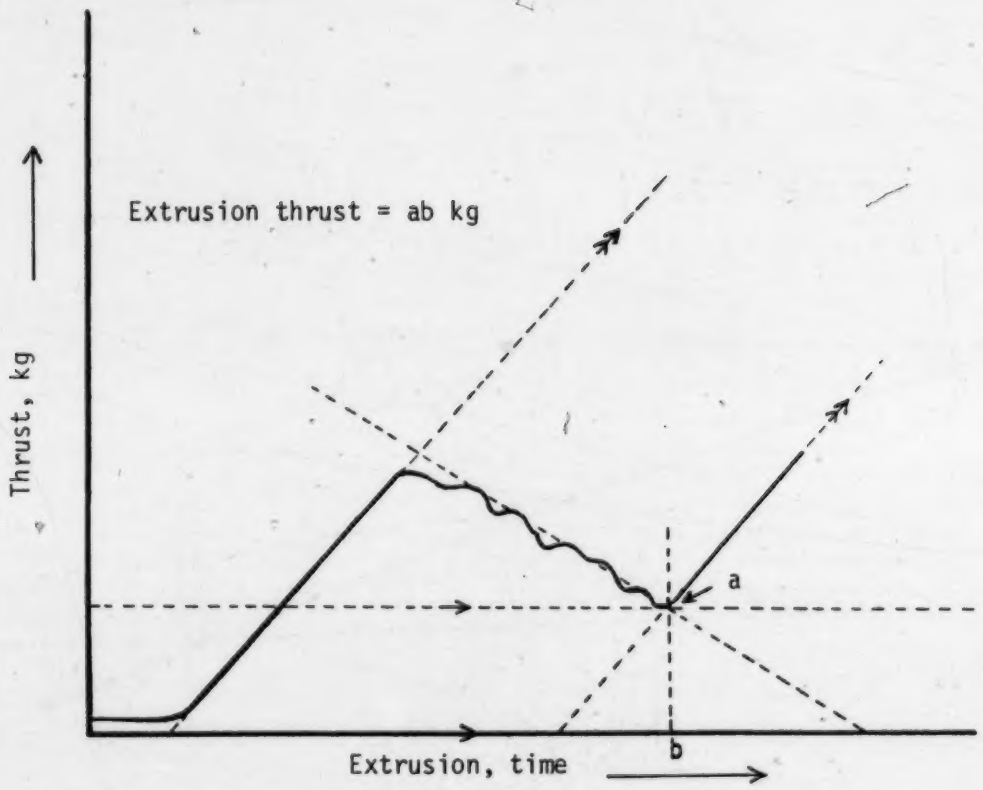


Figure 14. A typical thrust vs extrusion curve for the extrusion test.

4.6. AN IMPROVED PROCESS FOR EXTRUDED FRENCH FRY PRODUCTION.

The process of making extruded French fries was studies from several points of view, with the objectives of establishing an optimum water to granule ratio and of developing formulations that produced products with improved texture, eating quality and freedom from oiliness.

4.6.1. Materials.

Freeze-thaw and Add-back potato granules.

"Chipper". An extruded French fry mix.

Frozen par fries. I & S Produce Ltd., Edmonton, Alta.

Crisp film. National Starch Co. (Canada) Ltd., Boucherville, P.Q.

Textaid. National Starch Co.

Baka snak. National Starch Co.

OK Ceri-Gel. The Hubinger Co., Keokuk, IA.

OK Pre-Jel. The Hubinger Co.

'A' Clintose. Clinton Corn Processing Co., Clinton, IA.

Gelcarin, M-100. Algrin Corp. of America, Rockland, ME.

Sea Cor, SLC-2. Stauffer Chemical Co., San Fransisco, CA.

Na-CMC, 7HF. Dow Chemical Co. (Canada) Ltd., Sarnia, Ont.

Methocel, HG 90 or K-100. Dow Chemical Co.

Tetra-sodium pyrophosphate, food grade. Food Manufacturing Co. Ltd. Carteret, NJ.

Potato flavour. Bush Boake Allen Co. Ltd., London, England.

Supro 630. Ralston Purina Co., St. Louis, MO.

Guar gum, FG 70-70. Hercules Inc., Wilmington, DE.

Crisco soya-bean oil. Proctor & Gamble Co. (Canada) Ltd., Toronto, Ont.

4.6.2. Equipment.

Cornelius Automatic Mashed potato Dispenser, Model MP II, The Cornelius Manufacturing Co. Ltd., Anoka, MN.

Ilnes Extruder Machine, Model 6000. Ilnes Machine Products Ltd., Weston, Ont.

Modified Cookie-press.

Deep fat fryer. Canadian General Electric Co. Ltd., Montreal, P.Q.

4.6.3. Procedures.

4.6.3.1. Optimum Granule to Water Ratio.

In establishing the optimum granule to water ratio (w/v), fresh Freeze-thaw and Add-back granules were reconstituted with tap water at 2.1, 2.3, 2.6, 2.8 and 3.0 times their weight. The respective reconstitution times and extruder thrusts of the doughs thus formed were determined following the procedures described previously. These data, together with the handling and extrusion properties of the doughs subjectively evaluated by the author, were then compared to the values obtained for aged granules forming a satisfactory dough.

4.6.3.2. Additives.

The choice of additives depended on their functional properties and their compatability with potato granules in forming a potato dough that could be shaped into French fry strips of acceptable eating quality. However, the levels added were determined by means of trial and error.

4.6.3.3. Dough Preparation.

Initially, 50 g batches of a granule mix containing the additives under test were reconstituted by gentle stirring in water at an optimal ratio of 1:2.3 (w/v). After a 10 min setting period, the

dough was extruded through a cookie press modified to produce strips with a cross-section of 1 cm^2. The extrusion head was made of 1 cm thick Teflon sheet in which was cut a tapered hole 1.5 cm^2 on the inside and 1.0^2 on the outside; this shape was necessary to avoid ragged edges of the fries.

Later, the dough was prepared in 0.5 kg batches with an extruder apparatus which had been used institutionally. The French fry mix was poured into a cylinder containing the required amount of water and briskly mixed using a wire wisk.

4.6.3.4. Studies on the Automash Machine.

Studies were conducted to adapt the Automash Machine to automatically reconstitute French fry mixes. The Automash is presently being used in fast-food outlets to produce instant mashed potatoes by simultaneously dispensing granules and hot water at a certain rate and ratio into a vortex mixing chamber. In this manner small quantitles of granules and water are thoroughly mixed in a continuous stream before being discharged into a receptacle. Modifications were made such that the apparatus reconstituted French fry mix with cold water in a ratio to produce a satisfactory dough (Figure 15). After a 10 min setting period, the dough contained in a cylinder was placed in the extruder machine, and by means of a lever the dough was forced through an extrusion plate into the desired French fry shape (Figure 16). The fries were then cut and dropped into a fry basket (Figure 17). All products were fried in a vegetable oil for 90 sec at 185°C (Figure 18), and immediately evaluated by a taste panel for appearance, texture, flavour and overall acceptance.

Figure 15. The Automash Machine reconstituting the french-fry mix with cold water to produce a uniform dough.

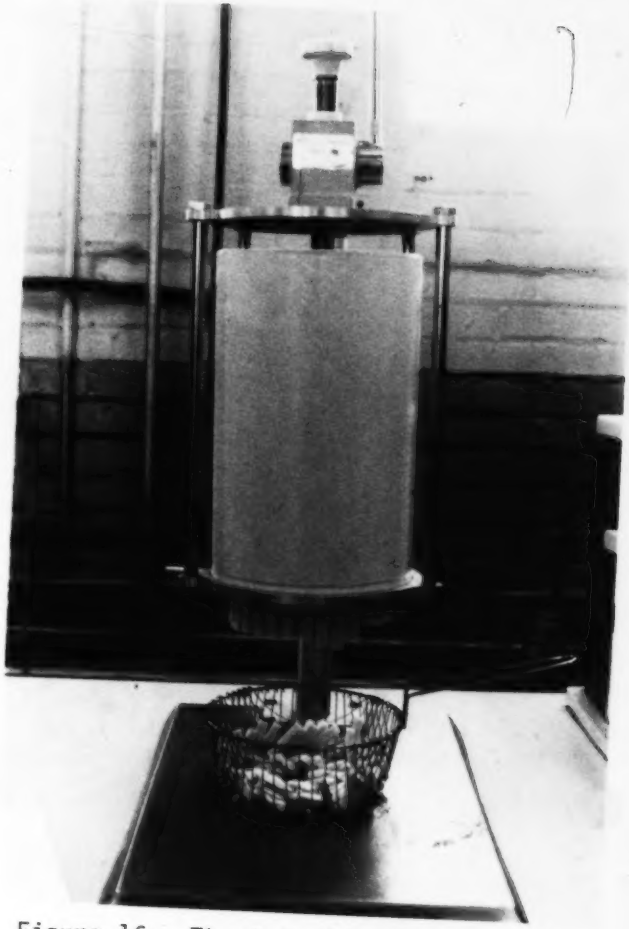


Figure 16. The extruder machine forming the dough into french-fry shaped strips.

Figure 17. The cut french-fry strips in a fry basket ready for frying.

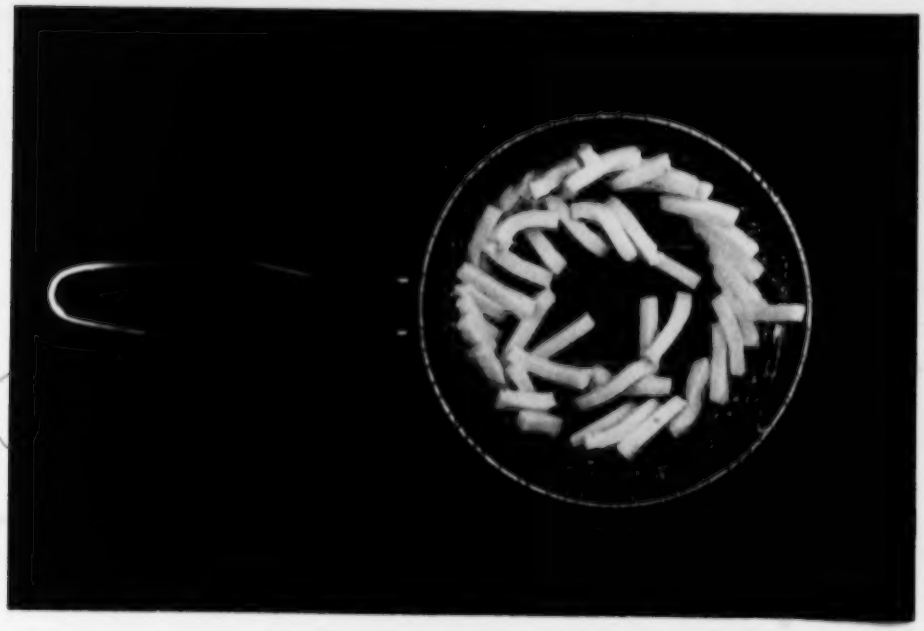


Figure 18. Extruded french-fries ready for consumption.

4.6.3.5. Proximate Analysis.

The yield, expressed as the weight of fries per unit weight of the dry mix, and moisture and oil contents of the fries were determined immediately after frying. The samples were dried in a vacuum oven (76 mm Hg) at 70°C to a constant weight (48 h). The dry solid was then extracted for 16 h in a Soxhlet apparatus using petroleum ether (b.p. 40-60°C) as a solvent. The ether extract was first evaporated using a vacuum rotary evaporator and then dehydrated twice with chloroform: methanol (2:1, v/v) followed by drying in vacuo for 6 h. Percent moisture and oil were expressed on the total weight (wet basis) of the fries and were an average of duplicate determinations done on three separate batches of each sample.

4.6.3.6. Taste panel Evaluations.

The organoleptic quality was initially determined by the author following the scheme shown in Figure 19, and was later confirmed by the use of difference-preference tast panel evaluations as outlined by Kramer and Twigg (1970). The 8 panelists were volunteers chosen from the staff of the Department of Food Science. For a given series of evaluations, four sessions were held on alternate days. The judges were given a scoring sheet on which explicit instructions for the scoring method (a 9-point hedonic scale) were given (Figure 20). Each judge was then served with coded samples on paper plates arranged in random order. The coding of the samples was also randomized in every session, using different sets of codes.

In the first series of evaluations, four formulae of extruded French fries (Table 1) were compared to par fries fried in oil at

Characteristics
Handfeel during mixing & dough preparation:- 0 = dry/crumbly/non-cohesive 10 = cohesive/correct moistness 15 = too wet/non-cohesive
Extrusion properties:- (i) strength: 10 = good; 0 = limp (ii) ragged edges: none = 10; excessive = 0 (iii) retains shape upon standing = 10; does not = 0
Frying properties:- (i) retains shape during frying = 10; does not = 0 (ii) disintegration during frying: none = 10; excessive = 0 (iii) explosion puffing: excessive or none = 0; correct = 10 (iv) air space: none = 10; excessive = 0
Characteristics of outside skin:- (i) texture: leathery or soggy = 0; crisp & flakey = 10 (ii) flavor: 10 - 0 (iii) color: golden-brown = 8 - 10; pale brown = 7 - 5; too dark = 4 - 0
Characteristics of inner core:- (i) texture: soft and pasty like A-B mash = 0 - 3 mealy like F-T mash = 4 - 7 firm like freshly mashed potato = 8 - 10 (ii) flavor: 10 - 0 (iii) oiliness: 10 - 0

Figure 19. A scheme for evaluating quality of extruded French fries.

DIFFERENCE-PREFERENCE TESTING OF FRENCH FRIES

Instructions:

I. Please give a score to each of the five (5) products presented. We are using a 1-9 point hedonic scale:-

9. Like extremely
8. Like very much
7. Like moderately
6. Like slightly
5. Neither like nor dislike
4. Dislike slightly
3. Dislike moderately
2. Dislike very much
1. Dislike extremely

II. When scoring the "overall impression", take into consideration properties you feel are important for the type of product under test, and explain in your comments. Include also the following characteristics:-

a. colour and appearance of the product

b. organoleptic properties of the outside skin based on

(i) Texture - crispiness/flakiness/toughness
(ii) Flavour - taste/aroma/fattyness

c. Organoleptic properties of the inside core based on

(i) Mouthfeel - pastiness, fattyness/firmness
(ii) Flavour - taste/aroma/fattyness

d. Overall impressions

III. When scoring either high or low, please explain your reasons. Any additional comments are most welcome.

IV. Salt is provided, sprinkle a small pinch evenly and please use it sparingly.

NAME: DATE:

Product type / Product characteristics					
a. Colour and appearance of the product.					
b. Organoleptic properties of the outside skin.					
c. Organoleptic properties of the inside core.					
d. Overall impression of the product.					

COMMENTS:

Figure 20. Scoring sheet for the taste panel evaluation of extruded French fries.

180°C for 3-4 min. In the second series, extruded French fries from two formulae using F-T granules (Table 2) were compared to "Chipper" (an extruded French fry mix at one time commercially available in Canada). The ingredient label of the "Chipper" product read as follows: dehydrated Netted Gem Potatoes (A-B granules), cornstarch, salt, vegetable gum, methyl cellulose, dextrose, vegetable glycerol monostearate, and sodium acid pyrophosphate, sodium bisulphite and butylated hydroxytoluene. Formula 1 in series II, found to be the most acceptable by the panelists, was fortified with 5% Supro 630, a soya protein isolate. The fortified and the non-fortified formulae were then compared in the final series of evaluations (Table 3).

The date obtained were analyzed using analyses of variance, and correlations with APL library programmes on an Amdhal 460 computer. The mean scores for appearance and colour, flavour and texture of the outside skin and inner core, and overall acceptance of the products were compared using Duncan's Multiple Range Test (Duncan, 1955). The variance ratios and coefficients of concordance indicated that the panelists generally performed best in the third of the four sessions held for each series of evaluations. Hence, for simplicity, only data from the third session in series II and III, and the fourth session in series I are presented.

Table 1. Extruded French fry formulae tested in Series I.

	Level of ingredient added (%)			
	FT I 1	FT I 2	AB I 1	AB I 2
F-T potato granules	100.0	100.0	-	-
A-B potato granules	-	-	100.0	100.0
Methocel HG 90 or K100 Premium	1.0	1.0	1.0	1.0
Na-CMC 7HF	0.5	1.0	0.5	1.0
Textaid	1.0	1.0	1.0	1.0
Crisp film	1.0	1.0	1.0	1.0
Baka Snak	0.5	0.5	0.5	0.5
OK Ceri Gel 443	0.5	0.5	0.5	0.5
OK Pre Jel	0.5	0.5	0.5	0.5
Gelcarin MR 100 or SeaCor SLC-2	0.5	0.5	-	-
Guar gum F-G 70-70	-	-	0.75	0.75
'A' Clintose	0.5	0.5	0.5	0.5

Table 2. Extruded French fry formulae tested in Series II.

	Level of ingredient added (%)	
	FT II 1	FT II 2
F-T potato granules	100.0	100.0
Methocel HG 90 or K100 Premium	1.0	1.0
Na-CMC 7HF	0.5	0.5
Textaid	1.0	5.0
Crisp film	1.0	3.0
Baka snak	0.5	0.5
OK Ceri Gel 433	0.5	0.5
OK Pre Jel	0.5	0.5
Gelcarin MR 100 or SeaCor SLC-2	0.5	0.5
'A' Clintose	0.5	0.5

Table 3. Formula for the protein-fortified extruded French fry mix tested in Series III.

	Level of ingredient added (%)	
	Fortified	Non-fortified
F-T granules	100.0	100.0
Methocel HG 90 or K100 Premium	1.0	1.0
Na-CMC 7HF	0.5	0.5
Textaid	1.0	1.0
Crisp film	1.0	1.0
Baka Snak	0.5	0.5
OK Ceri Gel 443	0.5	0.5
OK Pre Jel	0.5	0.5
Gelcarin MR 100 or SelCor SLC-2	0.5	0.5
'A' Clintose	0.5	0.5
Tetra Sodium pyrophosphate	0.5	0.5
Potato flavour	< 0.05	< 0.05
Supro 630	5.0	-

RESULTS AND DISCUSSION

5.1. SEM STUDIES OF THE POTATO GRANULE PROCESS.

5.1.1. The Add-Back Process.

An essential pre-preparation of potatoes for the A-B process is precooking at 70°C for 20 min and cooling in cold water prior to steam-cooking. This serves to render the cell wall less degradable by cooking (Bartolome and Hoff, 1972b), thereby enabling the potato cells to withstand the forces generated by compression, mixing and rubbing during the continuous mash-mising step (Potter et al., 1959). Figure 21 shows the potato tissue after precooking, cooling and steam-cooking. The intercellular space was created by partial solubilization of cementing materials. However, the cells were still firmly bound together in many places. Since the cementing materials in the CW and ML, essentially pectic substances, were only partially degraded, the CWs were stronger than those of the cooked cells without the pre-treatment where the solubilization was more complete (section 5.2.3.).

In the mash-mixer about two parts by weight of dry granules were recycled to be mixed with the freshly cooked tissue. Surfactants and antioxidants were also added at this stage. About half way through the mash-mixing step, which took approximately 25 min, there was still a considerable amount of dry granules which had not been mixed with fresh cells (Figure 22a). Those that were mixed appeared to be attached or embedded between the freshly cooked cells, thereby separating them out into single cells or aggregates (Figure 22b). As the mash-mixing proceeded more cells were separated. Due to rubbing action, the surface of the detached cells appeared smooth, and

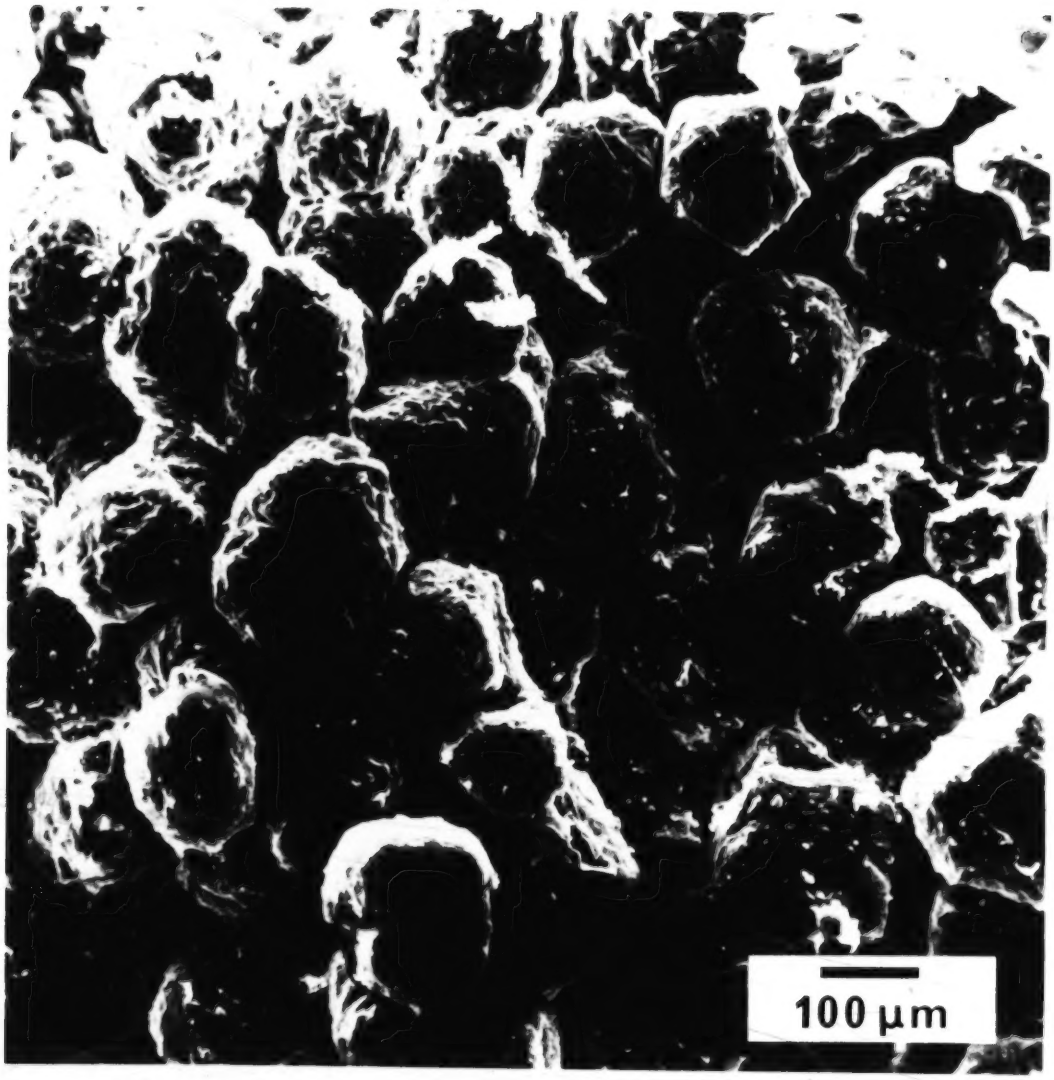


Fig. 21. Photomicrograph of pre-cooked, cooled and steam-cooked potato tissue in the Add-Back process. The cooked cells remain largely bound together by partially degraded cementing materials.

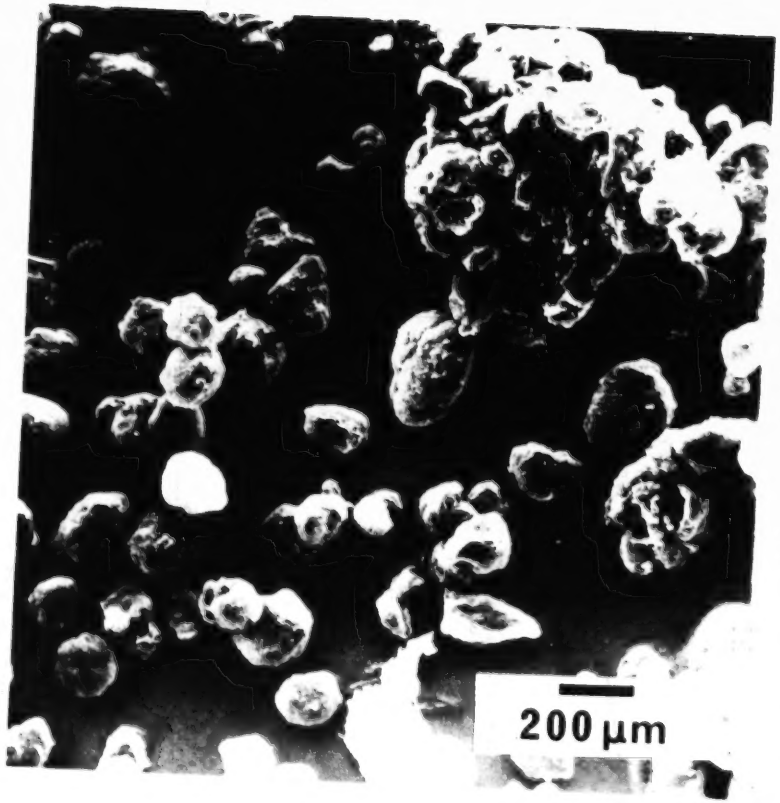


Fig. 22a. Photomicrograph of mash-mixed potatoes half way through the mash mixer of the Add-Back process. Most of the loose cells are the recycled dried granules.

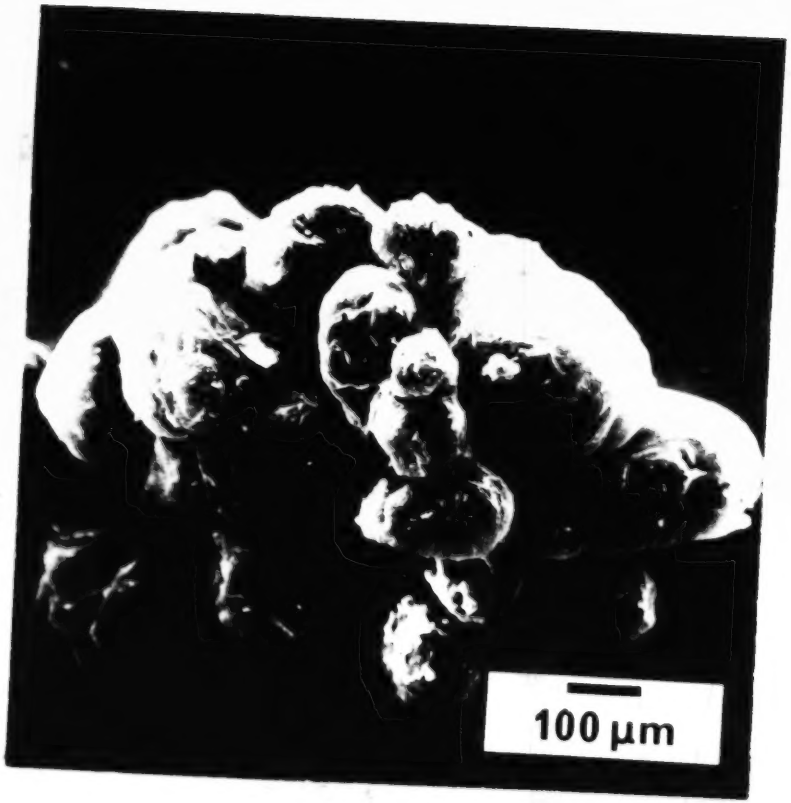


Fig. 22b. Photomicrograph of mash-mixed potatoes half way through the mash mixer showing some dried granules attaching to or embedded in the freshly cooked tissue.

some had released starch gel or cementing materials adhering to them (Figure 23).

After mash-mixing the product entered the conditioner where it was tumbled along a tunnel through which warm air at about 45°C was blown. The conditioning took about 45 min during which the starch gel partially retrograded (Potter et al., 1959) and the moisture content was reduced from 35% to about 31%. The product at this stage was still largely in form of single cells and cell aggregates (Figure 24). The potatoes were then charged into a fluff-mixer where cell aggregates or lumps were further separated to smaller units (Figure 25a). However some big, unbroken lumps still remained (Figure 25b). These lumps might be either freshly cooked potato tissue which was not separated during mash-mixing, or reunited cells which were bound together by starch gel released from damaged cells. They would be sifted out of the product as scalp (reject).

The product was dried in an air-lift dryer, where the moisture was reduced to about 15%, then in a fluid bed dryer and a cooler where the moisture was lowered to about 8%. The dried product was then passed through a series of sieves where the particles bigger than 10 mesh, consisting mainly of unbroken tissue or large aggregates (Figure 26), were discarded or sold as animal feed. Entrained particles in the dust collectors of the fluid bed dryer and cooler consisted mainly of very small granules, vascular materials, and dried starch particles (Figure 27). This material probably should be sold as animal feed but, for economic reasons, is often recycled. The intermediate sized particles (between 10 and 80 mesh) were recycled together with some final product to the mash-mixer. The final product (smaller than 80

Fig. 23. Photomicrograph of a new granule formed in the mash-mixer showing a relatively smooth surface with some released starch or cementing materials attached to it.

Fig. 24. Photomicrograph of potatoes at the end of the conditioning step showing the product which consists of new granules that may be single cells or cell aggregates, and some recycled granules (smaller in size).

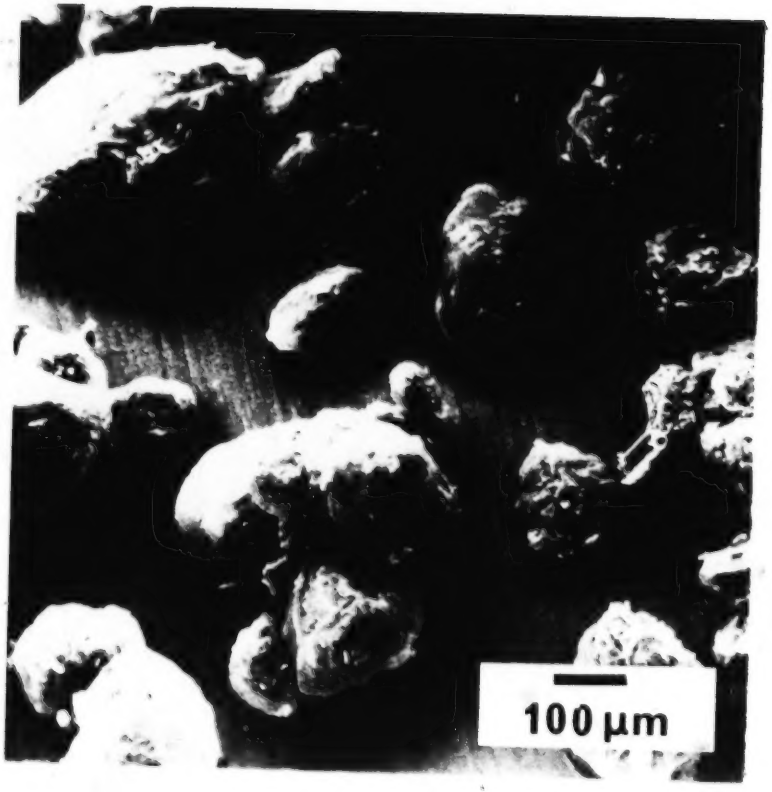


Fig. 25a. Photomicrograph showing potatoes coming out of the fluff-mixer that consist of single cells and cell aggregates.

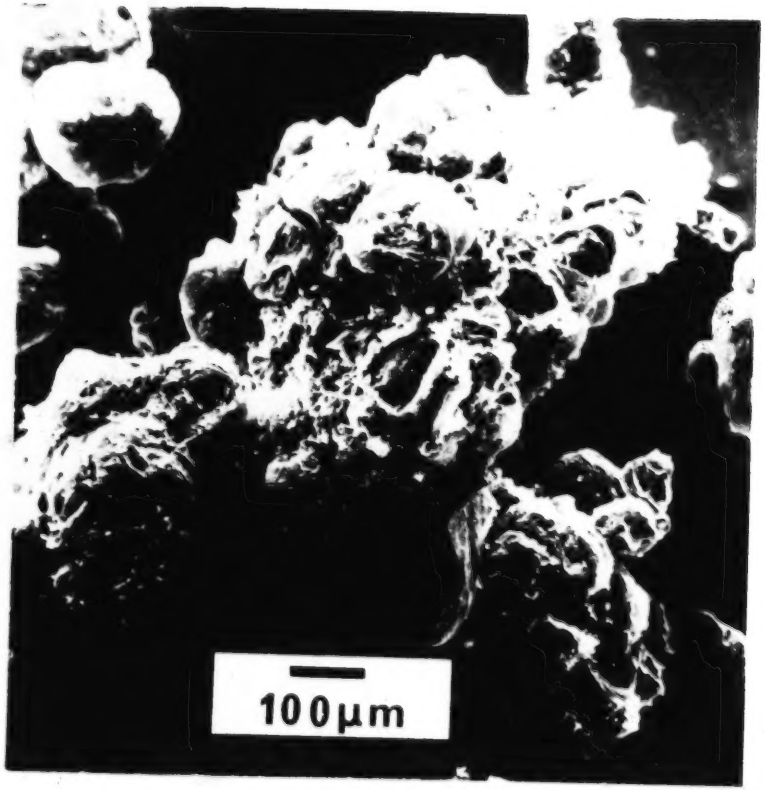


Fig. 25b. Photomicrograph showing unbroken lumps or cell agglomerates which remain after the fluff-mixing step of the Add-Back process.

Fig. 26. Photomicrograph of reject materials which remain on a 10 mesh sieve after the drying and cooling.

Fig. 27. Entrained particles from the dust collectors of the fluid-bed fluid bed dryer and cooler consisting of very small granules, vascular materials and dried starch particles.

mesh) consisted mainly of single cells and aggregates of a few cells (Figure 28a). Most granules were round and had fairly smooth surfaces, with CWs forming ridges and folds due to dehydration (Figure 28b). There appeared to be some tiny crystals over the surface (Figure 28c). They were thought to be chloride salt crystals (Fedec et al., 1977). Since some of the granules were damaged during the process, the starch matrix might be exposed, or starch released from one cell might be attached to another cell (Figure 28d), thus giving rise to glueyness in a reconstituted product.

5.1.2. The Freeze-Thaw Process.

In the F-T process the precook treatment was not applied. The potatoes were steam-cooked for 35 min and mashed hot (at a temperature not lower than 70°C) in a KitchenAid mixer for 1.5 min where most of the cells were separated from one another with very little damage. This was possible due to the fact that cooking alone caused more complete solubilization of cell binding materials, thus rendering the cells more easily separable (Figure 29). Figure 30 shows that, after mashing, the cells were detached from one another, while the CWs remained intact. Precooking was found to be detrimental to this process as it not only strengthened the CW but also rendered the cell binding materials less degradable, making it more difficult to mash without inflicting substantial cell damage (section 5.2.4.).

The mashed potatoes were then frozen in an air blast freezer at -29°C. As the potatoes were being frozen part of the intercellular water was drawn out osmotically due to the freezing concentration of the cell mass. Thus, ice crystals were formed both outside and inside the cells (Ooraikul, 1973), leaving most of the potato cells visibly

Fig. 28a. The final product of the Add-Back process consisting of single cells and cell aggregates smaller than 80 mesh.

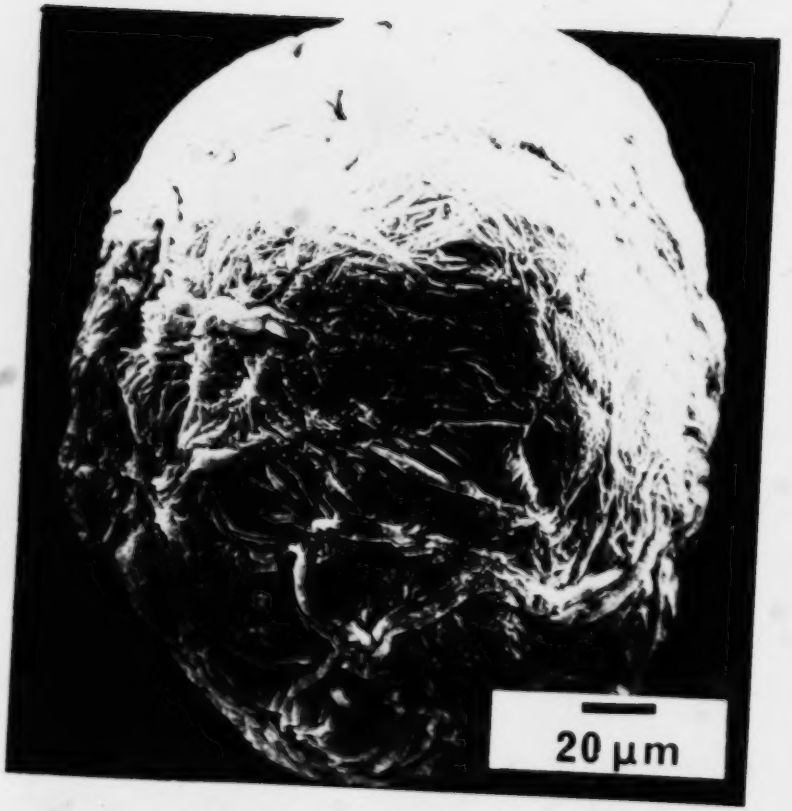


Fig. 28b. Photomicrograph of a single Add-Back granule showing a fairly smooth surface with ridges and folds.

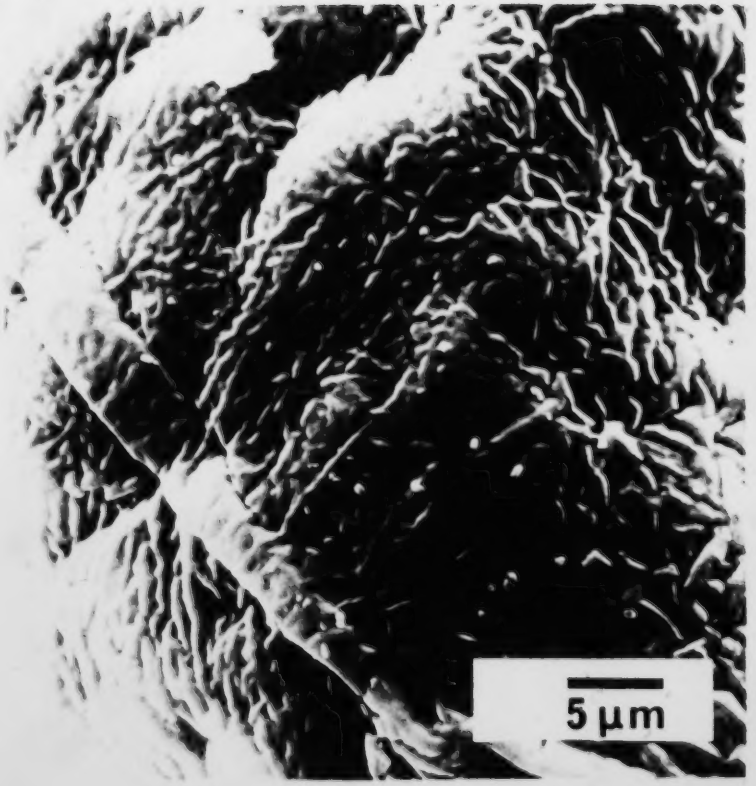


Fig. 28c. Photomicrograph of a close-up view of the granule surface with some salt crystals.

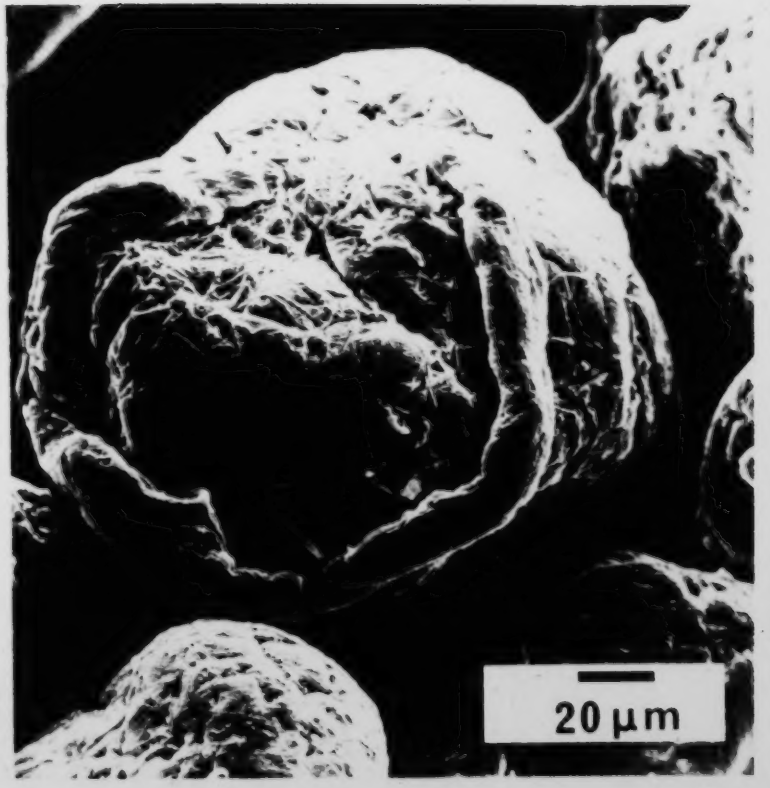


Fig. 28d. Photomicrograph of a damaged granule with exposed dried starch gel.

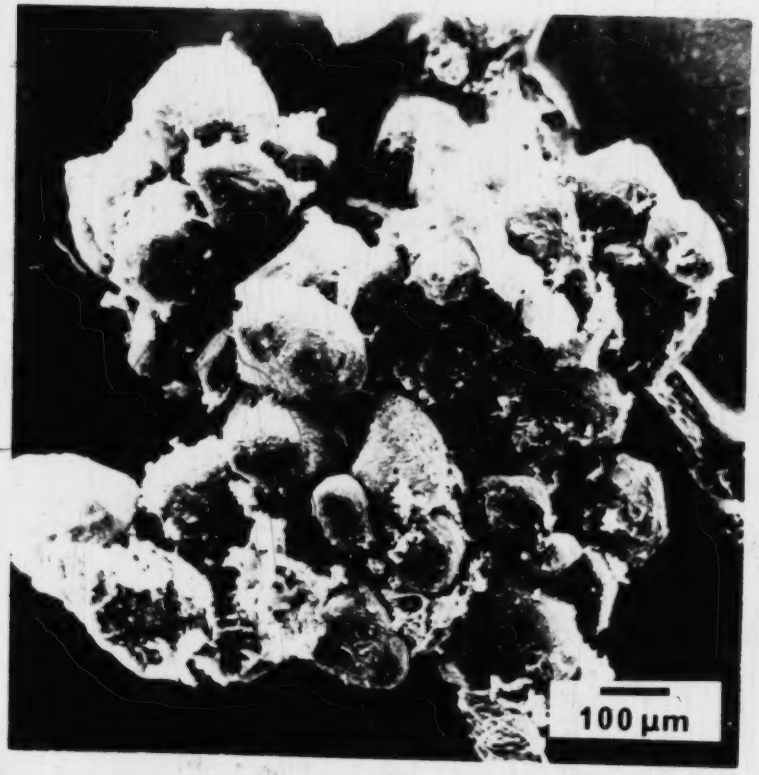


Fig. 29. Photomicrograph of steam-cooked tissue for the Freeze-Thaw process showing that the more complete solubilization of cell binding materials leaves a wide intercellular space which renders cell separation on mashing relatively easy.

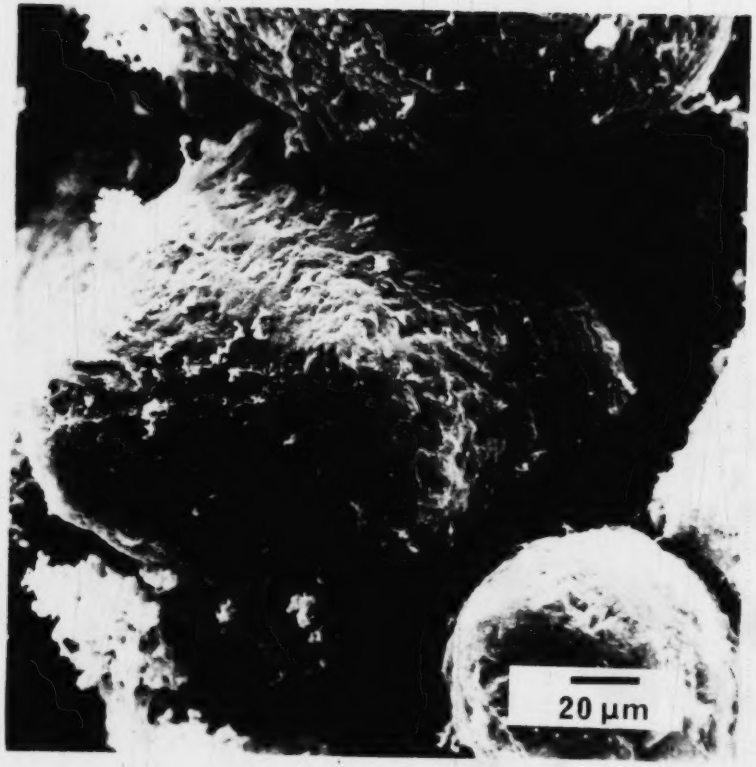


Fig. 30. Photomicrograph of detached cells after mashing in the Freeze-Thaw process showing that cell walls remain undamaged.

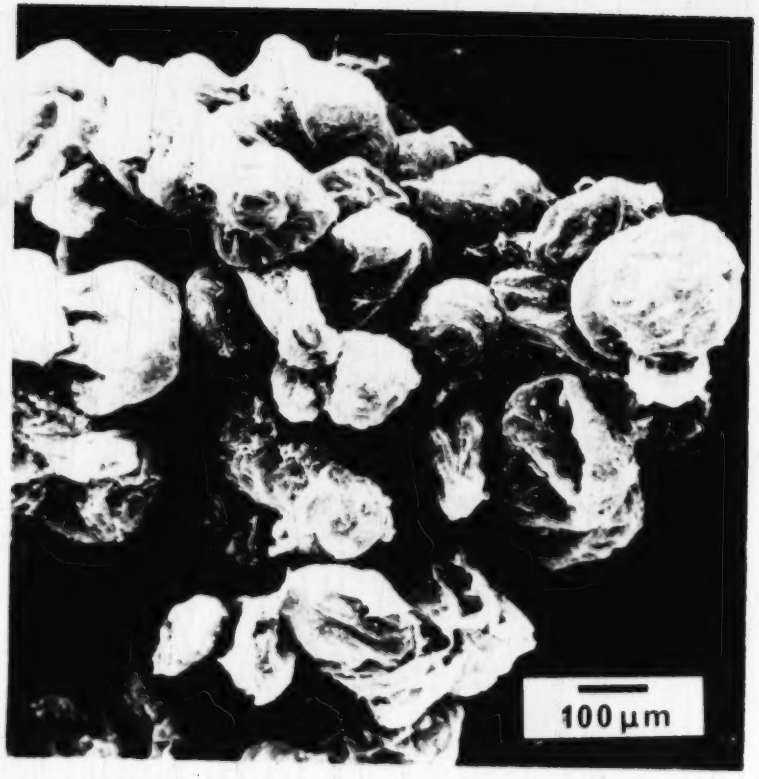
shrunken (Figure 31). The starch gel also retrograded more fully during freezing and thawing (French, 1959).

The frozen potatoes were thawed at room temperature to about 5°C. The surface of a frozen and thawed cell (Figure 32) showed its porous nature, most probably caused by ice crystals. These pores would have a profound effect on the drying and water reabsorption characteristic of the product.

When the thawed mash was predried for 10 min in a fluid bed dryer in an air stream of 65°C flowing at 130 m/min and with a stirrer speed of 30 rpm, the cells became progressively shrunken (Figure 33a) due to rapid loss of moisture, while the mash became increasingly free-flowing. Predrying, which lasted about 20 min, took place under a constant rate period of drying throughout (Ooraikul, 1978). This was made possible by the freezing and thawing, which not only drew a substantial amount of cellular water to the outside (Greene et al., 1948; Ooraikul, 1973), but also caused the cells to be more porous, making it much easier to transport the remaining water from within the cells to the surface during drying.

At the end of predrying the moisture content of the potatoes was reduced to about 40-45% and the mash was well separated into loosely bound aggregates of several cells (Figure 33b) ready for granulation. A close examination of the cell surface at this stage revealed the formation of wrinkles, ridges and folds (Figure 33c). This was due to loss of moisture and perhaps to the compressive force exerted by the stirrer and the potato cells themselves during the course of predrying.

After predrying, the potatoes were subjected to a relatively short period (10 min) of vigorous granulation under an air temperature and



Photomicrograph of frozen mashed potatoes showing cell shrinkage due to partial separation of water in the form of ice crystals.

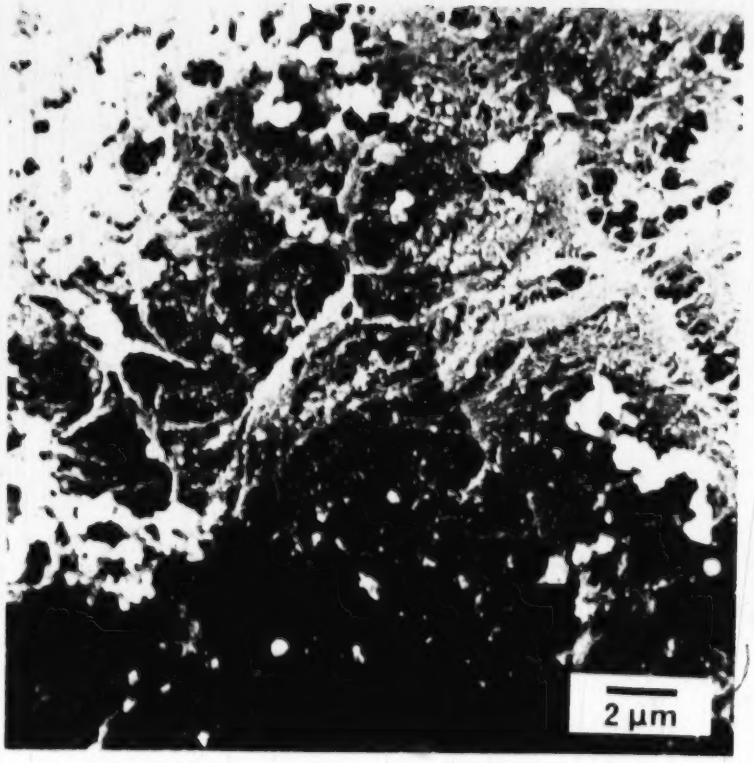


Fig. 32. A close-up view of the surface of a frozen and thawed [illegible] showing the porous nature of the cell wall surface caused by ice crystal formation.

velocity of about 25°C and 30 m/min, respectively, and a stirrer speed of about 400 rpm. During this time the moisture content of the potatoes was gradually reduced from about 45% to about 35%, while the cell aggregates were separated further to produce a finer product consisting largely of single cells and small aggregates of a few cells (Figure 34a). Note that most of the granules are shrunken and very angular in shape in comparison to the A-B granules which are largely round (Figure 28a). Under high magnification (2000x) the surface of the F-T granule was quite similar to that of the A-B granule, except that there appeared to be minute "craters" or "pin-holes" throughout the surface (Figure 34b) that were not observed on the latter. These craters could be caused by tiny holes formed by ice crystals puncturing the CW, and, hence, might serve as migratory passages for water and soluble materials. Some salt crystals were also apparent on the surface of the granules (Figure 34b), and they appeared to be larger than those on the A-B granules (Figure 28c).

Some potato cells were damaged during predrying and granulation, particularly in the latter stage where considerable force was generated by higher stirrer speed. The walls of some cells might be torn or the cells might be broken or sheared off (Figure 34c), exposing the starch matrix and, so, contributing to gluey texture on reconstitution. The damage may be considerable if granulation takes place when the moisture content of the potatoes is lower than 35%, which is the lower limit of the ideal range of 45-35% for granulation. Under ideal conditions, however, the damage should be low, not exceeding 3% broken cell count in the final product.

The granulated potatoes were dried in a fluid bed dryer at a temperature and velocity of 72°C and 115 m/min, respectively. The

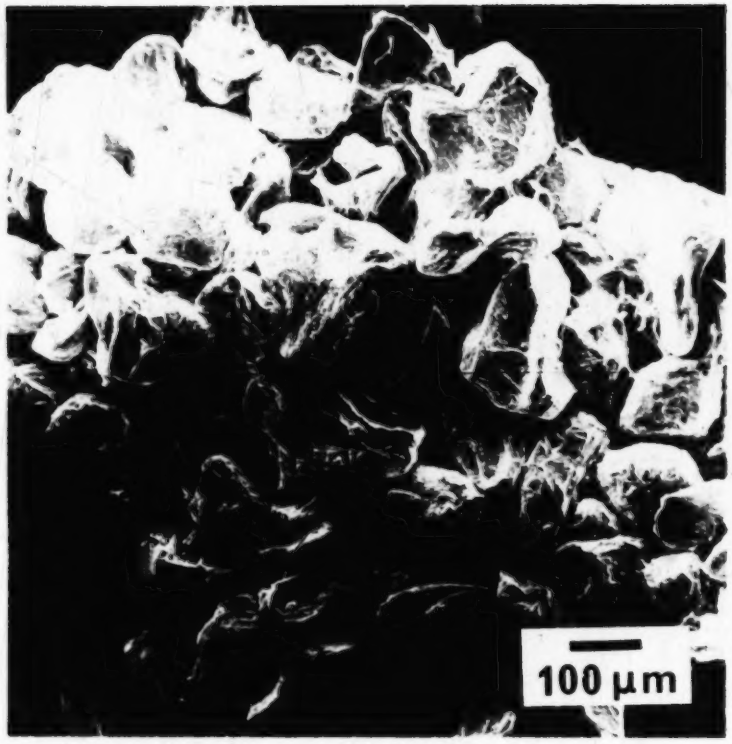


Fig. 33a. Photomicrograph of pre-dried (10 min) potato cells showing extensive shrinkage of the cells due to rapid dehydration.

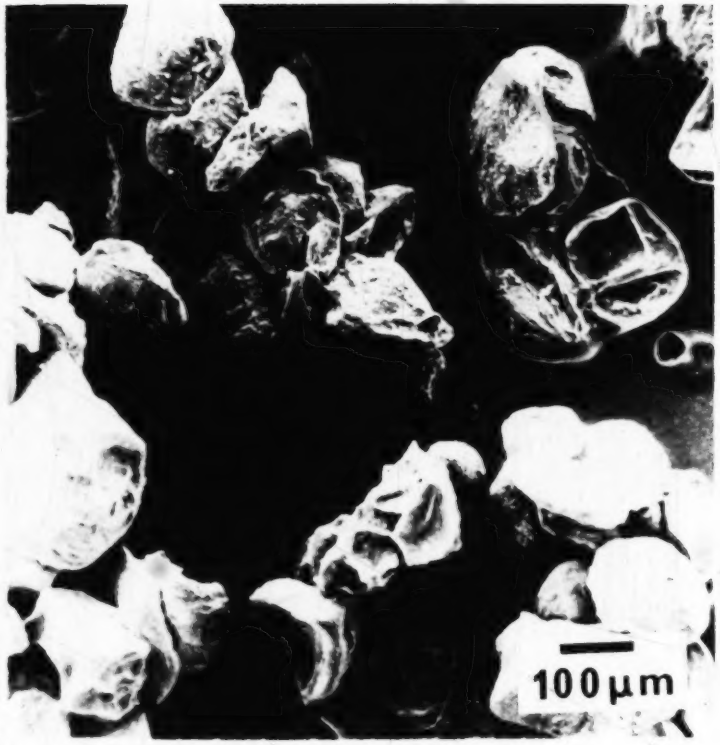


Fig. 33b. Photomicrograph of potatoes at the end of the pre-drying step of the Freeze-Thaw process showing loosely bound aggregates of cells ready for granulation.

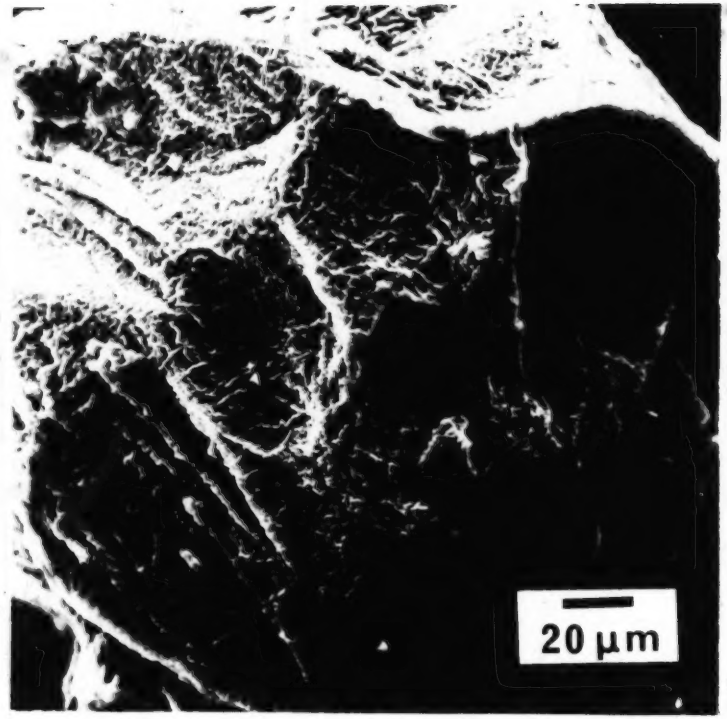


Fig. 33c. A close-up look at the surface of a predried cell showing wrinkles, ridges and folds.

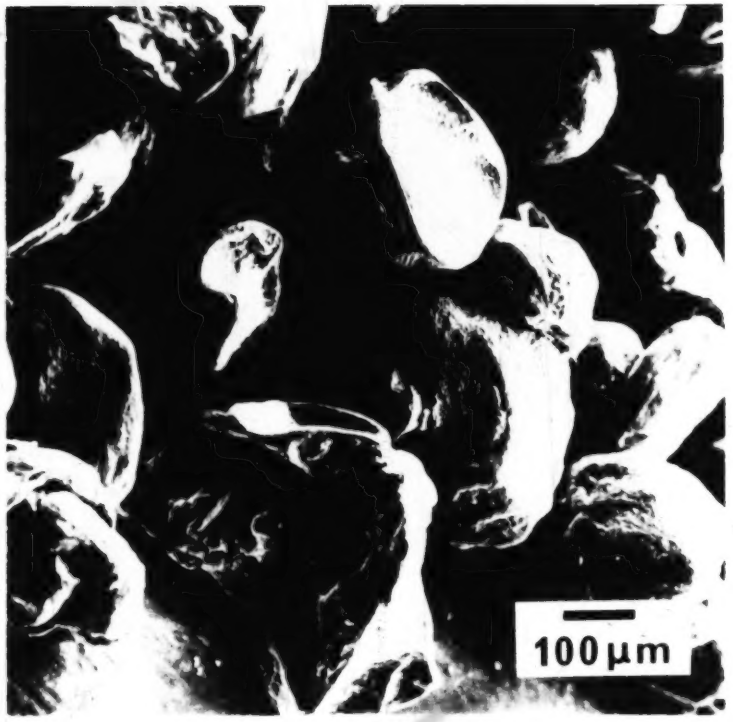


Fig. 34a. Photomicrograph of the Freeze-Thaw product after 10 min granulation showing granules consisting of single cells and small cell aggregates.

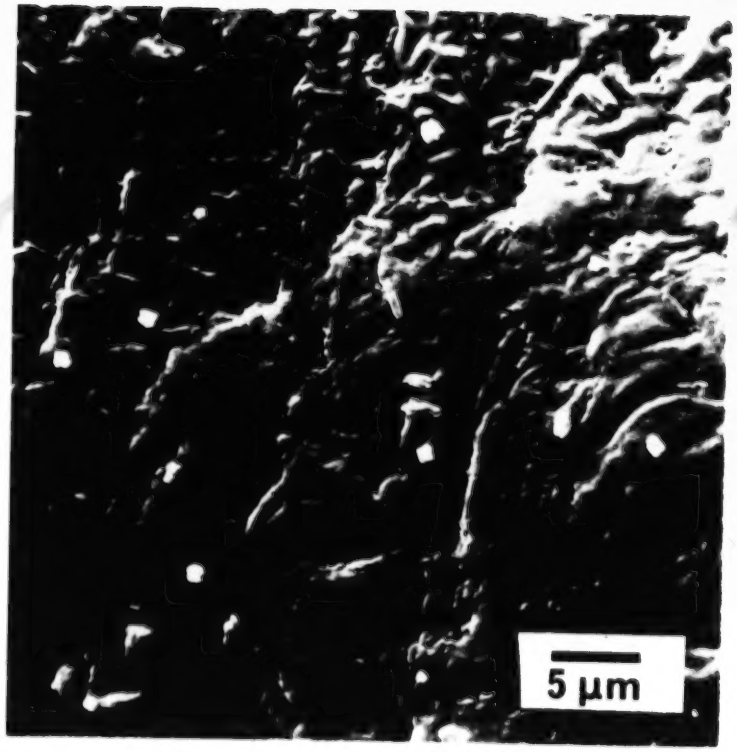


Fig. 34b. A close-up view of the surface of a Freeze-Thaw granule showing minute "craters" or "pin-holes" and salt crystals.

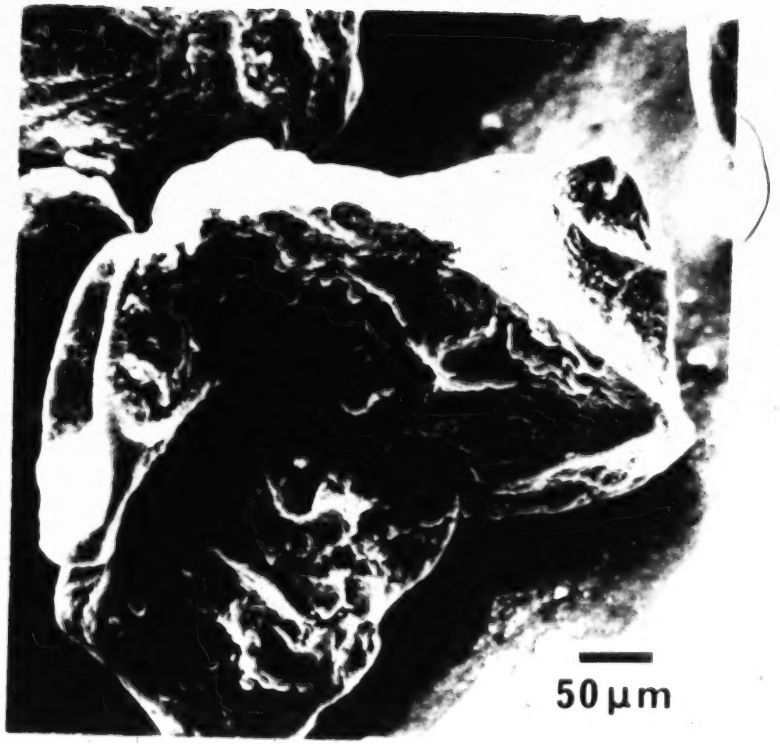


Fig. 34c. Photomicrograph of a damaged Freeze-Thaw granule. The granule might be sheared off during granulation exposing the starch matrix.

product was then passed through a series of sieves ranging from 18 to 60 mesh. Particles retained on 18 mesh consisted mainly of unmashable tissue (e.g. damaged tissue that was not trimmed), and reformed aggregates of several cells (Figure 35). The oversized aggregates were formed when released starch from damaged cells bound other cells so tightly together that even rigorous granulation failed to separate them. If granulation takes place when the moisture content of the potatoes is higher than the upper limit (45%) of the ideal range, this portion of the product could be considerable (Ooraikul, 1978). However, the reject portion should not exceed 2% under ideal conditions.

The intermediate size granules (smaller than 18 and bigger than 60 mesh) normally constituted not more than 10% of the total output. They consisted largely of aggregates comprising several cells which failed to separate during granulation, or which might have been reformed after granulation (Jericevic and Ooraikul, 1977). They could be reprocessed together with the freshly thawed potatoes without adversly affecting the process or the final product.

5.1.3. Comparison of the A-B and F-T Processes.

The difference between the A-B and the F-T processes lies essentially in the method of granulation. The A-B process requires the use of a considerable amount of dry granules to aid in the separation and in the reduction of the moisture content of the freshly cooked cells in the mash-mixer. During mash-mixing, where compression and friction are the predominant forces involved, the potato cells need to be strong in order to withstand those forces without sustaining excessive damage. This necessitates precooking and cooling treatment of the potatoes prior to final cooking. Furthermore, the mash-mixing step of

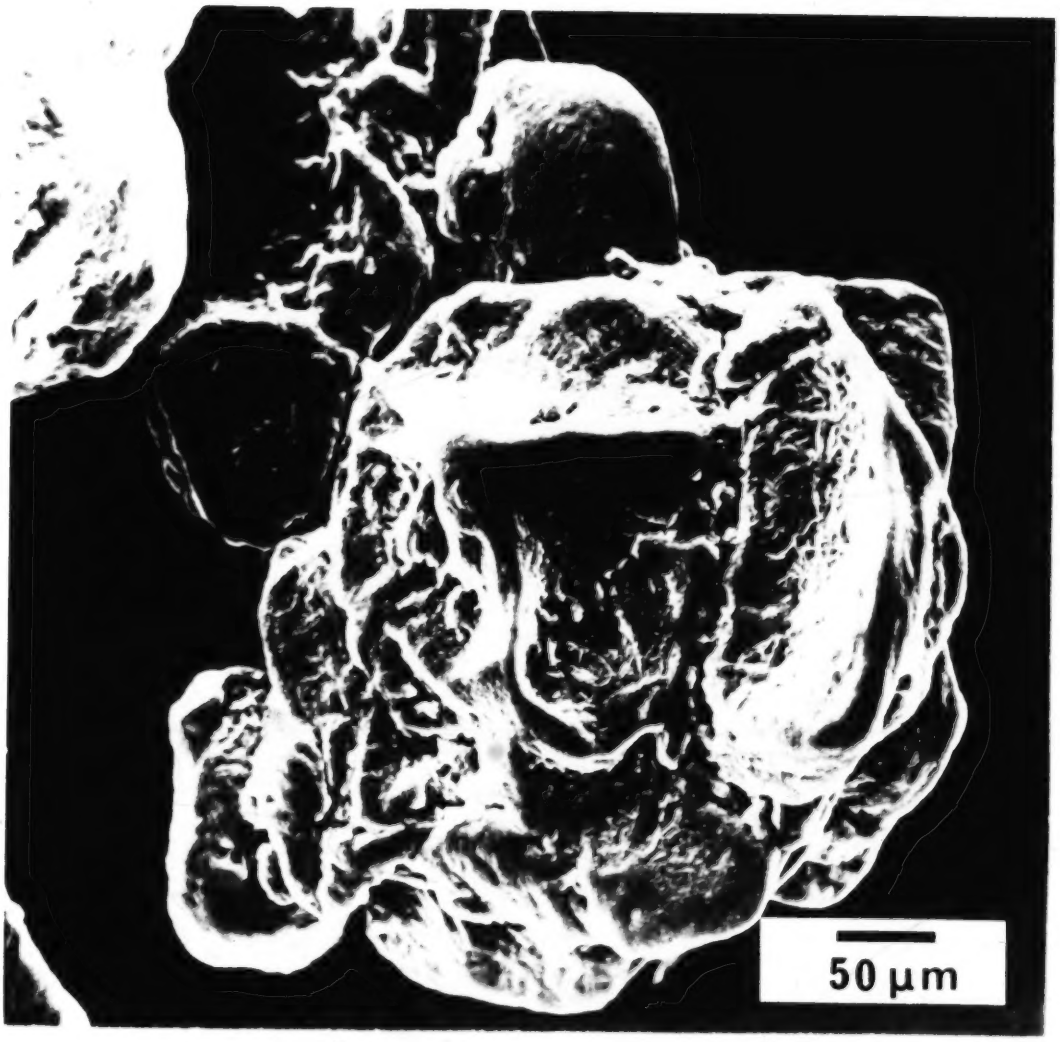


Fig. 35. Photomicrograph of an oversized particle (reject) from the Freeze-Thaw process. It appears to be an aggregate of several cells united together by starch gel released from damaged cells during pre-drying.

the operation requires 85-90% of the dried product to be recycled through the system (Gutterson, 1971). Most granules have to endure an estimated 8-10 processing cycles before they are packed out as product. Thus, accumulated physical and nutritional damage to the product can be quite considerable. The chance of one bad batch contaminating the following 8-10 cycles of the product is also substantial. Since additives, which include surfactants and antioxidants, are added at the mash-mixing step together with the recycled granules, the additives may not be uniformly distributed throughout the freshly cooked potatoes, resulting in a product with inconsistent quality and storage properties. For example, rancid off-flavour due to lipid oxidation often develops during storage or in transit, and only traces of antioxidants such as BHT are found in such granules (Pun and Hadziyev, 1978).

Since no freezing and thawing is involved in the process, however, the A-B granules tend to be more compact and round, resulting in a product of high bulk density (about 0.9 g/cm^3). This is desirable when the economy of packaging is considered. Round and dense granules also lend themselves well to automatic mashed potato machines, which are becoming popular in restaurants and institutions, where an individual serving of potatoes is produced by the push of a button. On the other hand, without freezing and thawing to induce somewhat drastic changes in physicochemical properties of gelatinized starch, the water reabsorption capacity of A-B granules tends to vary with the dry matter content of the raw potatoes used (Ooraikul, 1978).

The level of reject in the A-B product is also high, often more than 5%. There appear to be two major causes of the high reject.

Firstly, potatoes of different varieties and dry matter contents may require different combinations of precooking and final cooking times for effective cell separation on mash-mixing. Reeve (1967) states that precooked potatoes required longer cooking time than those not so treated, and that the effect of precooking may be "cooked out". On the other hand, undercooking may result in a considerable amount of hard, unbreakable pieces oftissue, left intact after mash-mixing, which will be sifted out as discard after air-lift drying. The second cause of the high reject is the release of starch gel from cells that were damaged during mash-mixing. This released starch may cause ball formation by binding other cells or aggregates into relatively large agglomerates (Figure 26) which will also be sifted out as discard. A high proportion of discard leads to considerable financial loss.

In the F-T process, the cooking technique is simple and straight forward. The only requirement is that the potatoes must be completely cooked. The cooked potato cells are effectively separated during mashing without much damage. The additives are introduced at this stage, and, since the mashing takes place at high temperature, they are readily incorporated and more uniformly distributed throughout the whole mash than in the A-B mash-mixing. Thus, the F-T granules would be more uniform in their properties than the A-B product. Effective cell separation on mashing would allow partial water removal from individual cells by ice formation on freezing. On thawing, this water remains largely outside of the cells, causing the mash to assume properties similar to those of granular materials such as wet sand. These properties are essential to quick water removal in the predrying step. Freezing also toughens cell walls (Greene et al., 1948), making

it possible to apply the stirring action in the predrying step to accelerate dehydration, and in the granulation step to further separate the cells without inflicting excessive damage. Freezing also accelerates the retrogradation of the starch gel (French, 1950) to near-completion, hence, optimizing the physicochemical changes in the starch matrix of the granules. Freezing causes a remarkable consistency in the water reabsorption capacity of F-T granules made from potatoes of different varieties or dry matter contents (Ooraikul, 1978). Thawing, however, must be controlled so that the temperature of the mash is not higher than 5-8°C when predrying starts or the benefit of freezing will be substantially lost through reabsorption of water and softening of cell walls.

Predrying and granulation are two of the most important steps of the F-T process, and require relatively precise control. These steps determine the amount of fine granules in the final product, the extent of cell damage, and the amount of discard. Excessively high temperature during predrying may heat up the product too rapidly before the moisture is reduced to a safe level of about 55%. A warm product reabsorbs water, and the cells tend to stick to one another. The ultimate result may be failure of the purpose of the predrying step, as the product would consist of balls of various dimensions that have a dry surface and soft centers and will not fluidize. This, however, is an extreme case. Well controlled predrying will produce a completely fluidized product of about 40-45% moisture content in about 18-20 min, depending on the initial moisture content of the potatoes.

Granulation should follow immediately. The control of air temperature and velocity is also crucial. If the temperature and velocity

of the air are too high, the moisture content of the potatoes will be reduced through the critical region of 40-45% before the product is completely granulated. This will result in a high proportion of intermediate size granules (between 18 and 60 mesh), and, probably, a high number of broken cells (Figure 34c). Proper granulation should be completed in about 10 min, when essentially all the granules are fluidized in the air stream of 30 m/min.

Due to partial separation of water from the cell during freezing and thawing and rapid dehydration during predrying, a considerable shrinkage of the cells occurs. This results in granules of angular shape and shrunken appearance (Figure 34a) which give rise to lower bulk density (about 0.80-0.85 g/cm^3) when compared with that of the A-B granules. The granule delivery system of the automatic mashed potato machine may need some simple readjustment to accommodate the F-T granules. F-T granules generally absorb water faster than A-B granules, perhaps due to the fact that angular granules have a bigger surface area per unit weight. Also, the surface of these granules appears to be covered with minute holes (Figure 34b) which may permit faster penetration of water.

Oversized granules (discard) appear to be produced by imcomplete mashing and/or improper predrying, where potato tissue is unmashed or small agglomerates of granules are formed with the aid of released starch from damaged cells (Figure 35). Under proper conditions the discard, consisting largely of unmashed tissue, is rarely higher than 1%, so there is a considerable saving over the A-B process.

5.2. EFFECT OF THE PRECOOK TREATMENT IN THE F-T PROCESS.

5.2.1. Processing Characteristics.

Predrying and granulation are the two most crucial steps in the F-T process (Ooraikul, 1978). Due to "ball" formation, the product obtained after precooking and cooling (Treatment I) could not be predried as successfully as that which had not been precooked (Treatment II). The product from Treatment I was doughy and gluey and tended to stick to the fluid bed. This prevented proper fluidization. When mashed, it contained many hard, unbroken pieces, often as large as 0.5 cm in diameter. This accelerated the formation of balls and resulted in an increase of reject material. Increasing mashing time from 1.5 to 2.5 min only reduced the size of these pieces without eliminating them, and made the mash more gluey, causing further problems in predrying.

Improper predrying led to further difficulties during the granulation step. The product at this stage contained many lumps which were dry and crusty on the outside and wet inside. This necessitated longer granulation periods than the normal 10 min at the expense of a higher percentage of broken cells, leading to further deterioration of the product's textural quality, as shown by data from Table 4.

The efficiency of the F-T process was improved by altering some of the normal parameters to obtain better fluidization and granulation. This was done by reducing the temperature of the drying air, and by increasing the air velocity, drying time and the stirrer speed (Table 5). The yield was improved by increasing the mashing time from 1.5 to 2.5 min as the potato cells were slightly better separated. The modifications of the processing parameters improved fluidization during the predrying

Table 4. Effect of precooking on the efficiency of the F-T process as indicated by yield, reject and broken cells.

Sample type	Processing parameters	% Yield (-60 mesh)	% Reject (+18 mesh)	% Broken cells
Treatment Ia	Normal F-T process, except 16 min granulation period.	38.3 ± 6.6	7.7 ± 0.7	9.0 ± 2.8
Treatment Ib	Normal F-T process, except 12 min granulation period.	55.1 ± 2.4	4.6 ± 0.1	10.5 ± 0.7
Treatment Ib	Modified, as explained in the text.	58.7 ± 2.0	4.3 ± 0.2	6.3 ± 1.2
Treatment II	Normal F-T process.	88.1 ± 6.0	0.9 ± 0.3	3.7 ± 1.2

Treatment Ia: Precooked, cooled and steam-cooked, and mashed for 1.5 min.

Treatment Ib: As Treatment Ia, except mashed for 2.5 min.

Treatment II: Steam-cooked only and mashed for 1.5 min. Values are means of at least two process runs.

Table 5. Some process parameters for the F-T technique using potatoes receiving the precook treatment.

Process parameter	Pre-drying 18-20 (15-18) min	Granulation 12 (10) min	Final drying 10-15 (10-15) min
Stirrer speed (rpm)	20 (30)	600 (400)	0 (0)
Air velocity (m/min)	200 (130)	30 for 5 min & 15 for 5 min (30 for 8 min & 50 for 2 min)	90-100 (115)
Air temp (^{o}C)	55 (60-65)	25 (25-32)	72 (72)

Data are for a 2.5 kg load.

Figures in parentheses are for normal F-T process.

and granulation steps, resulting in further improvement of the yield (Table 4). However, when compared to the normal process where the potatoes were steam-cooked without precooking, the yields of batches with the precook treatment were unacceptable. Furthermore, the amounts of reject and broken cells in these precooked products were unacceptably high. This appears to be due mainly to the fact that precooking strengthens the CWs (Bartolome and Hoff, 1972b) without weakening the binding force between the cells, resulting in rupturing of the cells when shear and compression forces are applied during the mashing, predrying and granulation steps.

On the other hand, strengthening of the CWs is desirable in the A-B process, as cell separation is accomplished by adding approximately two parts of dry granules to one part of cooked potatoes, and mixing and rubbing the dry particles against the cooked wet tissue for about 30 min under the action of rotary beaters. If the CWs were not toughened by precooking, mash-mixing would cause excessive mechanical damage to the cells, thus releasing free starch. This would not only make the succeeding stages of processing more difficult, but would also produce an inferior product (Harrington et al., 1959; Olson and Harrington, 1955).

5.2.2. Objective Textural Measurement of Intact Tissue and of Mashed Products.

Trial runs for compression tests showed the expected variation in firmness of different parts of the potato tuber. It appeared, however that samples taken from the inner phloem region of similarly sized tubers minimized this variation. To further reduce the variation, samples

from each position were cut in half, and treated as described. The results shown in Table 6 indicate that intact potato tissue receiving the precook treatment is firmer, and requires more compression force (1.37) than a product without the precook treatment (1.17).

These results are in agreement with those reported elsewhere (Bartolome and Hoff, 1972b; Olson and Harrington, 1955; Potter et al., 1959). However, when precooked and steamed potatoes were mashed, even for an extended period of time, the mash was not mealy and fluffy as other reports had suggested. In fact the mash had a doughy appearance and mouthfeel, which indicated excessive cell damage. Glueyness measurements presented in Table 7 show that precooked and steam-cooked potatoes mashed for 1.5 min exhibited about three times more glueyness than the steam-cooked sample. An attempt to further separate the cells by increasing mashing time from 1.5 to 2.5 min resulted in even greater cell damage, as shown by twofold increase in glueyness.

5.2.3. Pectic Substances.

Uronide contents of potatoes cooked with and without the precook treatment are presented in Table 8. Statistical analysis shows that there is no significant difference ($p < 0.01$) in the water- and calgon-soluble pectic substances of raw and of precooked potatoes. In fact, when the amount lost in the precooking water is taken into account, the water-soluble fraction of the precooked tissue is approximately the same as that of the raw tissue. However, raw and precooked potatoes have a lower water- and calgon-soluble pectic content than the precooked and steamed tuber, which in turn has less of these pectic fractions than the sample with only steam-cooking. This may suggest that pectic substances in potatoes are mainly in tightly bound forms

Table 6. Effect of precooking on the firmness of intact potato tissue as measured by a compression test.

Type of treatment		Position on tuber*								Grand Avg.**
		1	2	3	4	5	6	7	8	
I. Precook, then steam-cooking.	Avg. area under curve***	1.45	1.27	1.38	1.46	1.46	1.32	1.29	1.35	1.37
	S.D.	0.22	0.25	0.29	0.25	0.28	0.19	0.24	0.31	
II. Steam-cooking only.	Avg. area under curve***	1.53	1.17	1.19	1.18	1.19	1.11	1.14	1.20	1.17
	S.D.	0.23	0.25	0.26	0.28	0.24	0.23	0.27	0.27	

*See Figure 3.
**Significant at p = 0.01.
***Each value is an average of 10 replicates, in an arbitrary unit of a planimeter.

Table 7. Effect of precooking and of mashing time on the firmness and glueyness of fresh and reconstituted mashed potatoes.

	Firmness		Glueyness	
	Mean*	S.D.	Mean	S.D.
1. Steam-cooked; 1.5 min mash. (fresh)	0.843[a]	0.112	0.013[a]	0.005
2. Precooked & steamed; 1.5 min mash (fresh)	0.922[a]	0.113	0.033[b]	0.007
3. Precooked & steamed; 2.5 min mash. (fresh)	0.743[b]	0.073	0.073[c]	0.005
4. Steam-cooked only; 1.5 min mash. (reconstituted)	0.785[c]	0.037	0.075[d]	0.010
5. Precooked & steamed; 1.5 min mash. (reconstituted)	0.852[d]	0.049	0.247[e]	0.024

*Means are the average of 12 observations for samples 1, 2 and 3, and 6 observations for samples 4 and 5 in the arbitrary unit of a planimeter. Sample means followed by the same letter are not significantly different at $p = 0.01$.

Table 8. Effect of precooking on water-, calgon- and HCl-soluble pectic substances of potatoes.

Treatment type	uronide content (mg/100 g dry matter)*						
	(i) Loss in the cooking liquor	(ii) water-soluble	(iii) calgon-soluble	(i)+(ii)+(iii) apparent total	(iv) HCl-soluble	(ii)+(iv) Total	(Total - apparent total)
1. Raw	-	154.4 ± 22.8[a]	101.4 ± 8.6[a]	255.9 ± 17.3	1157 ± 79.6	1311.7 ± 82.1	-
2. Precooked	39.9 ± 8.1	120.7 ± 14.2[a]	87.9 ± 13.5[a]	248.5 ± 6.3	-	-	-
3. Precooked and steam-cooked	39.9 ± 8.1	633.3 ± 32.5[b]	129.9 ± 13.3[b]	803.2 ± 25.6	-	-	508.5
4. Steam-cooked	-	1106.5 ±106.6[c]	201.0 ± 22.9[c]	1307.5 ± 86.9	-	-	-

*All values, expressed as $\bar{x} \pm S$, are an average of 8 determinations done in duplicate. Values followed by the same letter are not significantly different at $p = 0.01$.

and that only the temperature of cooking brings about their substantial dissolution.

The results in Table 8 show that solubilization of pectic substances was less in precooked potatoes than in those not precooked. The difference in uronide content of 508.5 g/100 g dry matter between the apparent total of the precooked and cooked tissue and the total of the raw tissue suggests that almost one third of the pectic substances in potatoes are not solubilized after precooking and cooking. On the other hand, the difference between the apparent total uronide content of steam-cooked tissue (1307.5 ± 86.9) and the total of raw tissue (1311.7 ±82.1) is insignificant. This implies that practically all pectic substances were converted to soluble forms by cooking without the precook treatment, rendering the steam-cooked cells less tough and much more easily separable than those receiving the precook treatment.

Bartolome and Hoff (1972b) proposed that Ca^{2+} and Mg^{2+} from the cell interior diffuse to the CW at precooking temperatures and react with the increased amount of free carboxyl groups of the CW pectins obtained as a result of PME activation at above 50°C. The ionic linkages so formed would then render the CW pectins more resistant to further thermal degradation. However, in this study precooked and steamed intact tissue was firmer and less separable into single cells than tissue steam-cooked alone. This suggested that, like the CW, the ML could also easily be involved in such biochemical changes. Though limited knowledge exists about pectins of the ML compared to those of the CW, the results indicate that the ML was also rendered less degradable after precook treatment. A study by transmission electron microscopy (Chung et al., 1978) of butanol-treated potato cells showed that the

thickness of ML was only 0.13±0.6 μm. It was sandwiched between two adjacent CWs, each of 0.56±0.18 μm. These results might then suggest that ion diffusion into the CW and/or enzyme activation within the CW would also involve the thin ML. This would account not only for the lesser dissolution of pectic substances (Table 8) but also for all the results experienced in the F-T process wherein the cooked tissue had to be subdivided into single cells or small aggregates.

The above suggestion might be supported by Linehan and Hughes (1969b). They established a significant statistical correlation between intercellular cohesion and the calgon-soluble pectin fraction that is thought to be the "intercellular cement", i.e., ML. As found by Keijbets and co-workers (Keijbets and Pilnik, 1974b; Keijbets et al., 1976), the pH of the potato tuber is suitable for pectin degradation by a mechanism of depolymerization known as β-elimination. They found that a potato CW preparation (58% esterified pectic galacturonan), when converted into less esterified pectin, increases its binding capacity towards Ca^{2+}. Also, their finding that Ca^{2+} ions have a large capacity to insolubilize and stablize the pectin structure of the CW during boiling for 30 min, even when pectin alone might be progressively depolymerized, could be equally valid for pectins of the ML. This suggestion is in agreement with the present findings as well as those of Hughes et al. (1975). The latter authors also proposed that the degree of solubilization of the pectic lamella responsible for intercellular cohesion is responsible for potato texture.

5.2.4. Scanning Electron Microscopy.

Precooking induced hydration, swelling and gelatinization of starch, as shown in Figure 36. The appearance of the cells as loosely

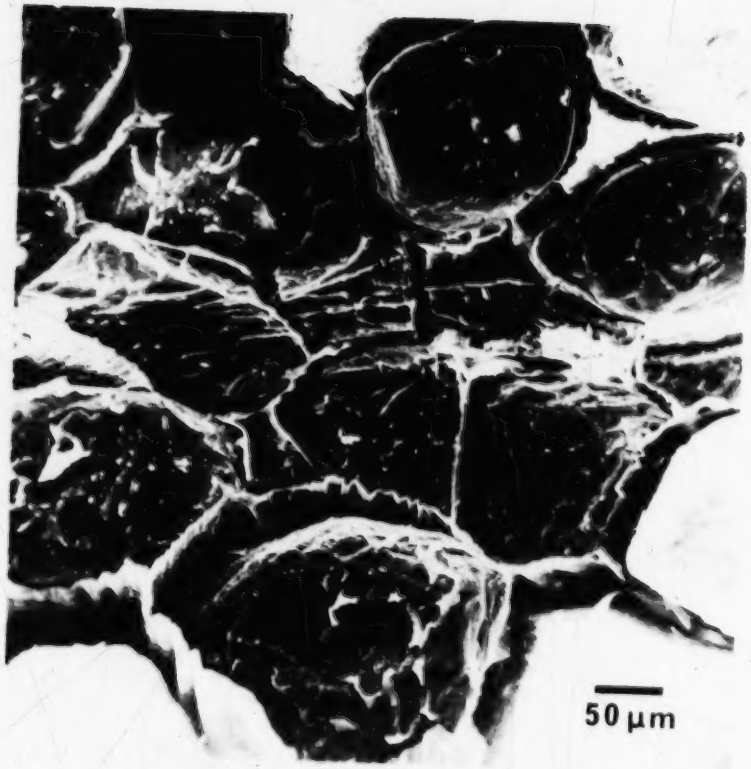


Fig. 36. SEM photomicrograph showing the gelatinization induced by pre-cook treatment. The gelatinized starch does not entirely fill the cell cavity and the cell walls do not indicate separation.

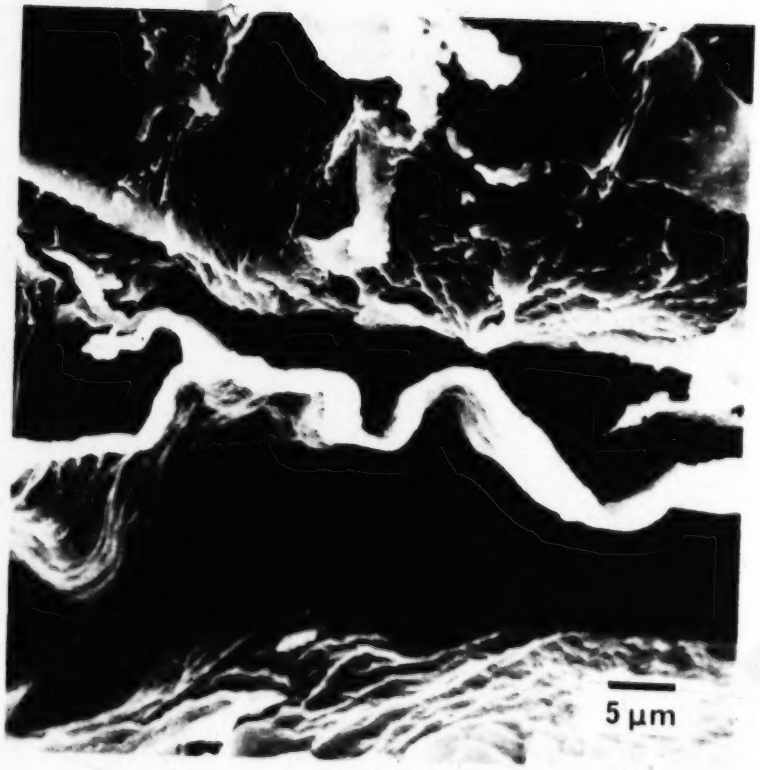


Fig. 37. SEM photomicrograph showing that cell walls from adjacent cells are still bound tightly to one another.

filled could be due to the presence of cytoplasmic materials, such as protein, between gelled starch and CW, rather than to the incomplete gelatinization of starch. The cytoplasmic material was removed by ethanol dehydration during SEM sample preparation, leaving space between the starch matrix and the wall. The CWs did not appear to separate from one another, indicating that the intercellular binding material was essentially undegraded by precooking alone. The walls were in fact bound tightly to one another as shown on the close-up view in Figure 37.

When the precooked tissue was steam-cooked, some solubilization of the cell binding material occurred (Figure 38). However, the cells were still closely bound together, as shown on the cross-section photomicrograph of the cells (Figure 39), whereas, in the steam-cooked sample without the precook treatment, they appeared well separated (Figure 40). This indicated that the ML in the latter was better solubilized, allowing the cells to become readily detached from one another. The precooked and steam-cooked cells, on the other hand, did not fully round-off and, hence, the expansion force was not strong enough to overcome the force exerted by the intercellular binding materials which might remain, in some cases, in the form of bridges interconnecting the cells (Figure 41).

When the precooked and steam-cooked tissue was mashed, many cells were not separated. This resulted in a mash consisting largely of cell aggregates rather than single cells (Figure 42). Much of the CW sustained extensive damage, thereby exposing the starch matrix and contributing to the glueyness of the mash. Even after freezing and thawing, the cells remained in the form of such intact aggregates (Figure 43).

After the thawed mash was predried for 10 min, the cells appeared

Fig. 38. SEM photomicrograph of pre-cooked and steamed tissue, showing some solubilization of cell binding material.

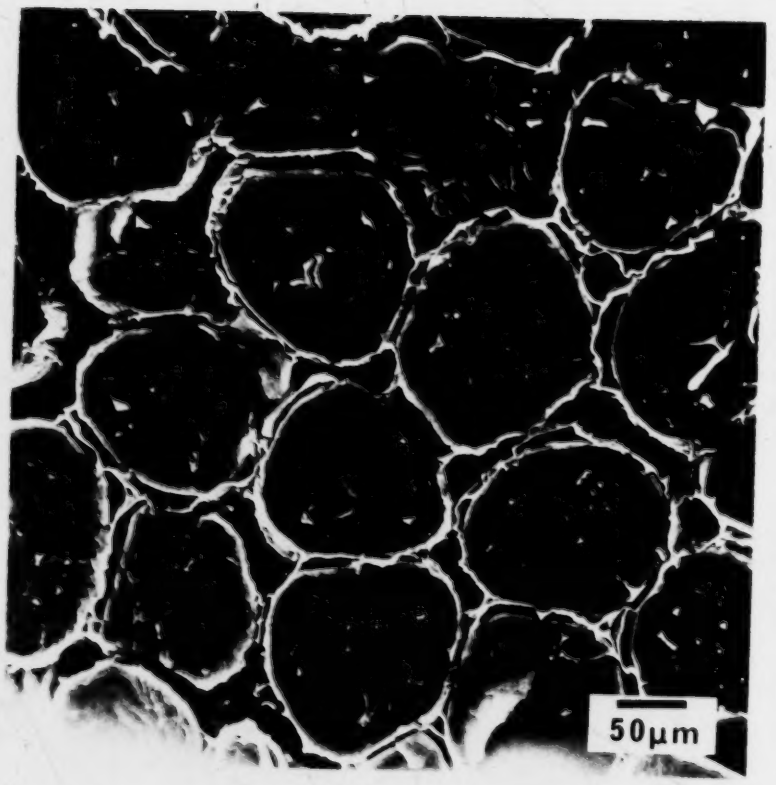


Fig. 39. A cross section of pre-cooked and steamed tissue showing that the cells are still largely bound to one another.

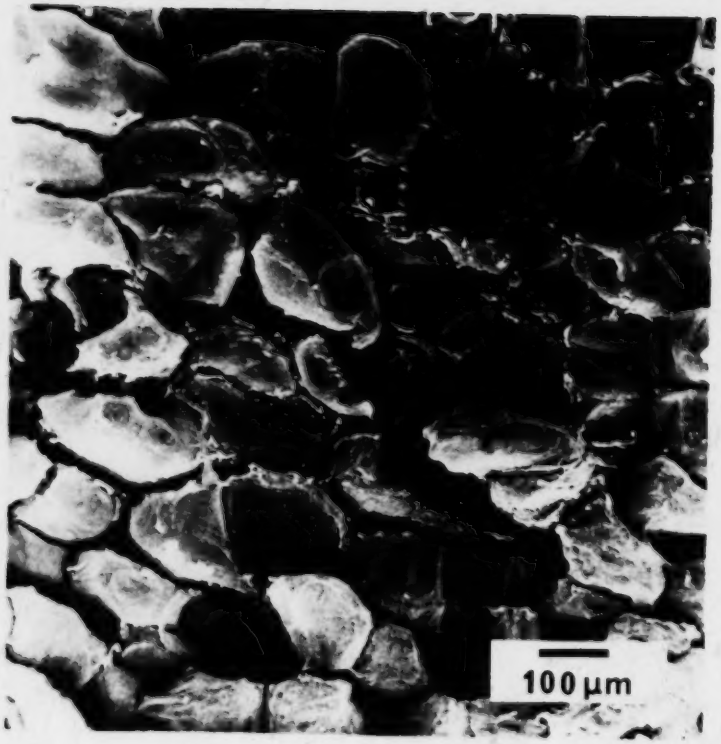


Fig. 40. SEM photomicrograph of steam cooked tissue without the pre-cook treatment, showing that the cells are well separated.

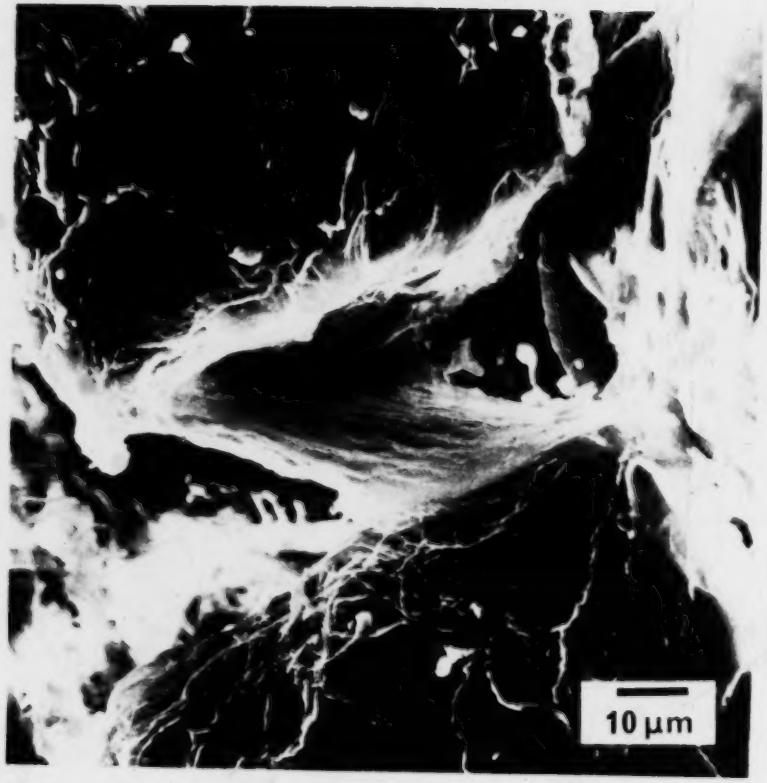


Fig. 41. SEM photomicrograph showing two cells joined by a leftover bridge of cementing material.

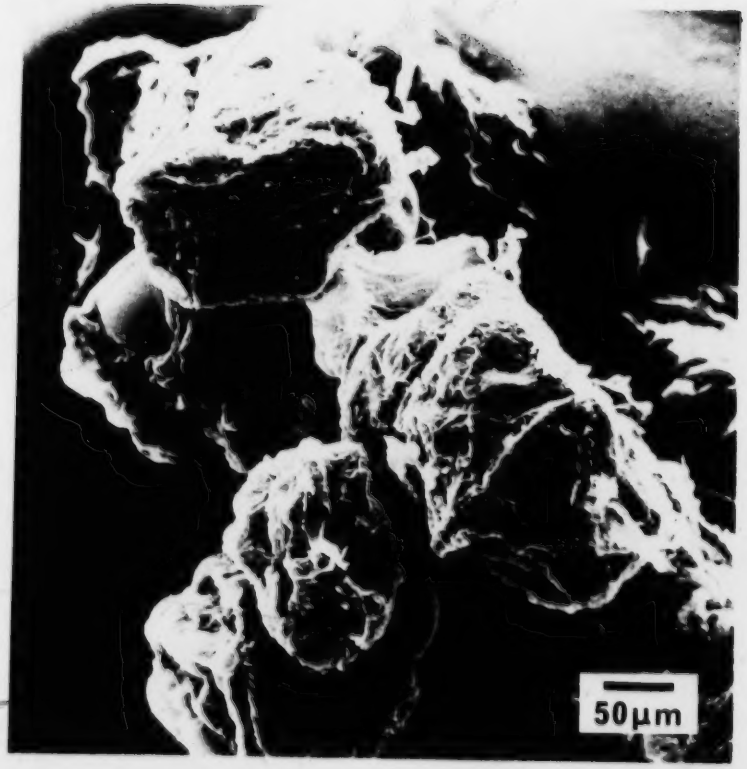


Fig. 42. SEM photomicrograph of pre-cooked and steamed tissue after mashing, showing unseparated cells as cell aggregates.

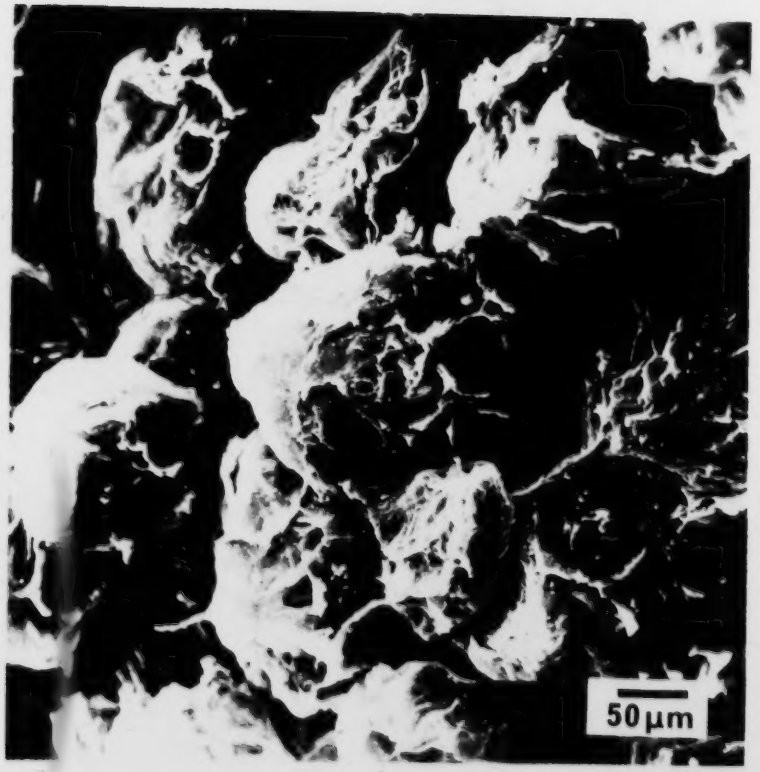


Fig. 43. SEM photomicrograph of the pre-cooked and steamed tissue after mashing, freezing and thawing, showing that the cells still remain in aggregates.

shrunken due to moisture loss, but most remained tightly fused to each other (Figure 44), rendering fluidization very difficult. After 10 min of granulation with the stirrer in the fluid bed running at a high speed of about 600 rpm to supply rigorous shearing and compression, some of the aggregates were reduced in size. However, the majority of the particles were still in the form of tightly bound aggregates of several cells (Figures 45 and 46). This resulted in a low yield of the final product (<60 mesh particles).

Thus, SEM study of precooked potatoes being processed with the F-T technique appeared to support other data that the precook treatment may be highly detrimental to the F-T proce-s.

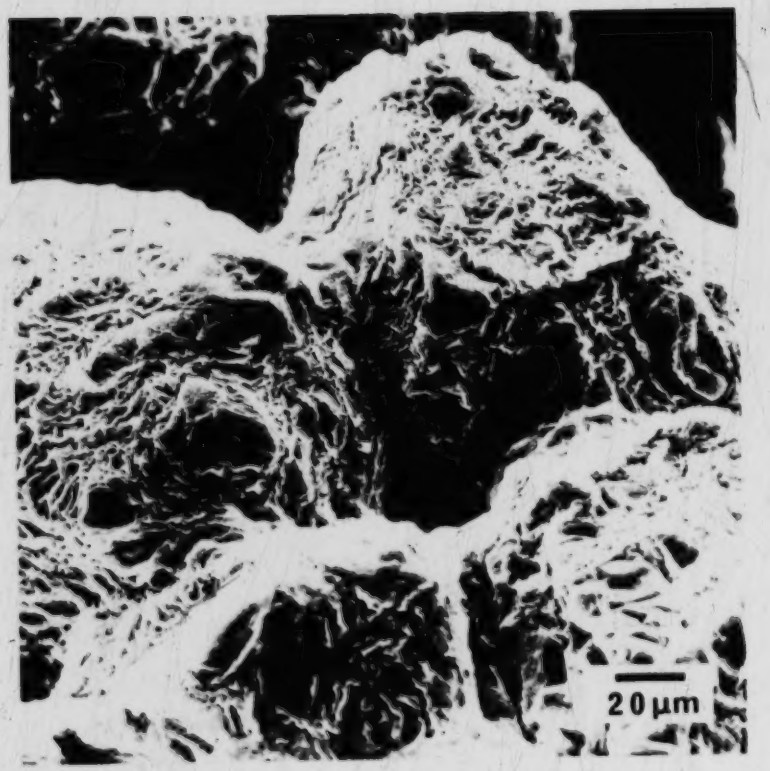


Fig. 44. Tissue from Fig. 43 after 10 min of pre-drying showing an aggregate of fused cells.

Fig. 45. SEM photomicrograph of the product after 10 min of granulation showing that the majority of the particles were still in the form of fused aggregates of several cells.

Fig. 46. SEM photomicrograph showing a close-up view of one fused aggregate.

5.3. MODEL STUDIES ON THE ROLE OF PME, CATIONS AND STARCH IN THE FIRMING EFFECT ON THE PRECOOK TREATMENT OF POTATO TISSUE.

5.3.1. Enzyme Assay of PME.

The principle of the method developed by Kertesz (1955) was considered to be the most suitable for PME assay. The method involves measurement of the rate of the reaction in which PME de-esterifies pectin, thereby increasing the free carboxyl group content of the reaction mixture. The pH is held at the optimum value by continuous addition of NaOH solution, and the alkali consumption is measured as a function of time. The amount of carboxyl groups set free in unit time is a measure of enzyme activity.

5.3.1.1. Enzyme Extraction Procedure.

The effect of NaCl concentration and the volume of the extracting medium on the amount of enzyme extracted is shown in Figures 47 and 48. The best extraction was obtained when the ratio of fresh potato to extraction medium (1M NaCl) was 1:2 (w/v), therefore, that ratio was used throughout.

5.3.1.2. Evaluation of the method for PME Activity Determination.

Preliminary experiments indicated that the reaction rate was dependent on the total volume of the reaction mixture, and the concentrations of substrate, enzyme and NaCl. Also, the activity was linear only if the alkali consumption was between certain limits. This could be due to a decrease in substrate and enzyme concentration caused by the addition of large amounts of alkali during PME determination. According to Vas et al. (1967), lower activity and irregular course of reaction are to be expected when using low NaOH concentrations. In the procedure adopted where the reaction mixture consisted of 4 ml of

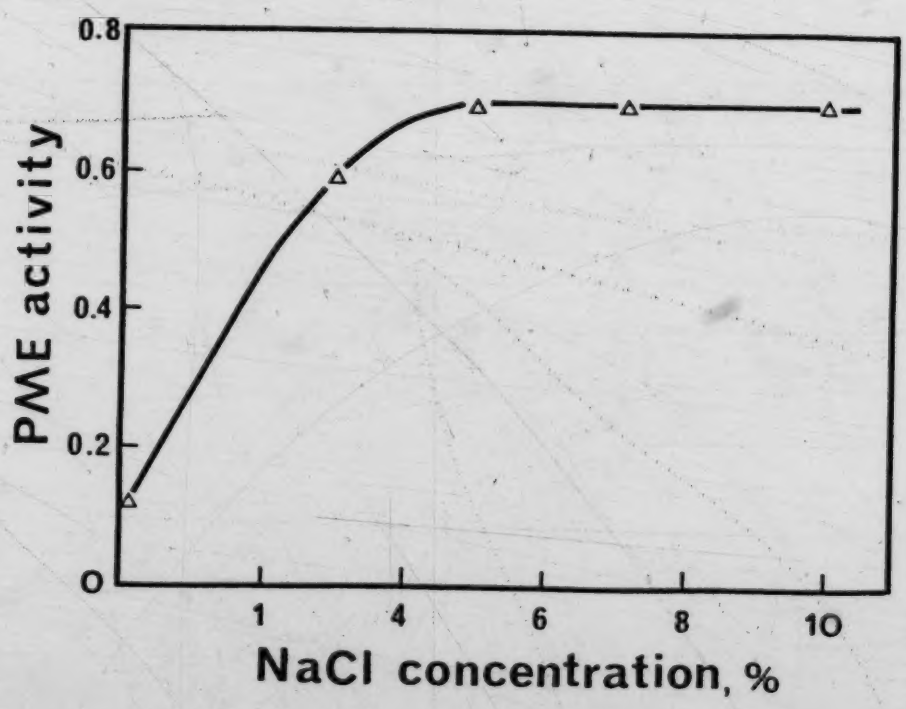


Figure 47. Effect of NaCl concentration during enzyme extraction.

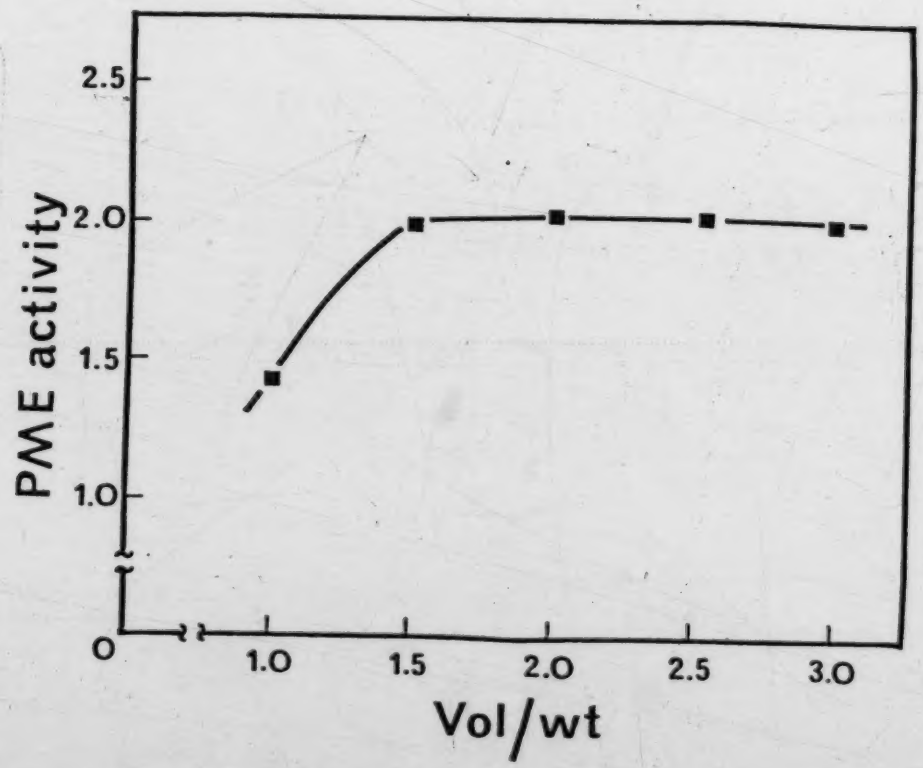


Figure 48. Effect of extractant volume on PME activity.

0.6% pectin solution and 2 ml of the enzyme extract, the activity remained linear for a period of 20 min when the consumption of 0.01M NaOH was 2 ml or less.

5.3.1.2.1. Effect of substrate concentration.

By varying the pectin concentration between 0 and 0.5% at a constant enzyme concentration, PME activity was shown to depend slightly on the concentration of the substrate, higher levels tending to give somewhat increased de-esterification rates (Figure 49). Thus, to ensure that the substrate concentration did not become a limiting factor and to maintain a linear activity rate for at least 15-20 min, 0.4% pectin was found to be the most suitable.

5.3.1.2.2. Effect of enzyme concentration.

Optimum activity was obtained when the reaction mixture was comprised of 2.5 ml enzyme extract and 3.5 ml pectin polution. Since higher amounts of enzyme would require greater alkali consumption, a mixture of 2 ml extract and 4 ml pectin solution was considered more desirable. Large amounts of the extract would also result in a high NaCl level. This would have an inhibitory effect on PME activity (Vas et al., 1967).

Concentration of NaCl in the reaction mixture was not adjusted, and varied from 0.5 to 3.0%. The differences in enzyme activity might be attributable to this, since Vas and co-workers (1967) showed a dependence of PME activity on NaCl concentration. This was confirmed by a later study where a concentration range of 1.5-2.0% NaCl was found to be optimal.

5.3.1.2.3. Effect of NaCl concentration.

Since fairly high levels of NaCl are necessary to desorb and

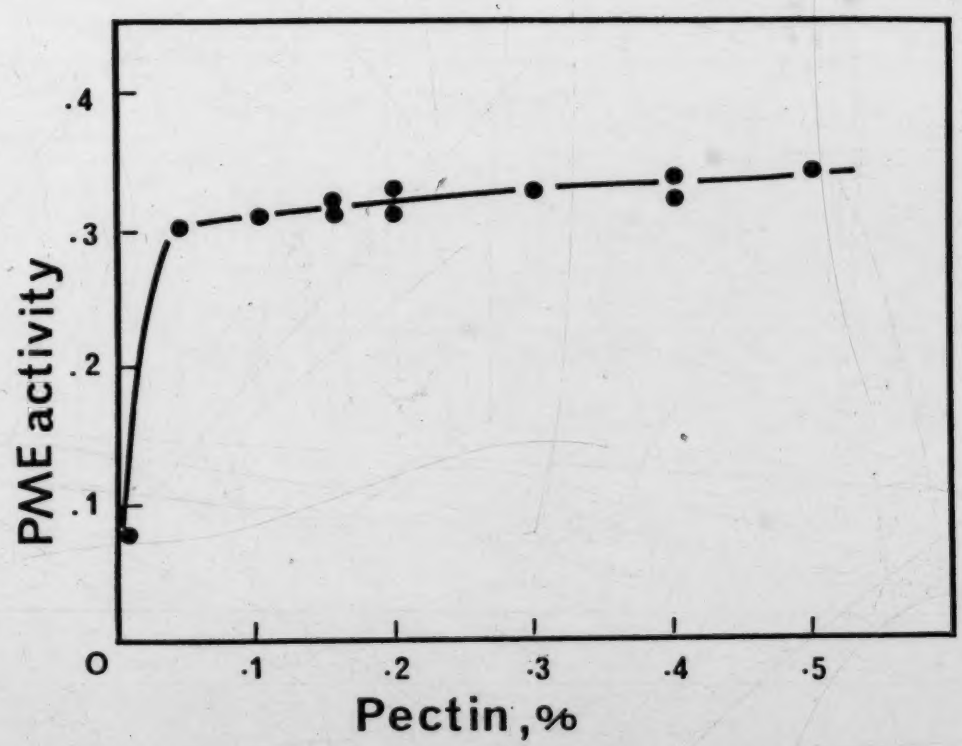


Figure 49. Effect of substrate concentration on PME activity.

solubilize PME, it was considered necessary to establish the effect of NaCl concentration on the enzymatic reaction rate.

The optimum concentration was between 1.5-2.5% NaCl (Figure 50). Concentrations higher than 3% had a definite inhibitory effect on PME action. This was taken into consideration in developing the enzyme extraction procedure and in establishing the amount of enzyme extract to be used.

5.3.1.2.4. pH and temperature optima for PME activity.

It was found that the optimum pH (Figure 51) and temperature (Figure 52) for enzymatic de-esterification of pectin were 7.0 and 60°C, respectively. However, in the final method of PME assay a pH of 7.5 and a reaction temperature of 30°C were chosen since these values are becoming widely accepted for the determination of PME activity.

5.3.1.2.5. PME activity in freeze-dried potato and CW/ML.

PME activity, expressed as µM carboxyl groups released per min at 30°C, for raw fresh and freeze-dried potato, and CW/ML, was, 9.72, 9.27 and 2.34 E.U. per g dry matter respectively. This was based on the moisture content of the samples and on a previous finding that, on a dry matter basis, potato had 5.1% CW/ML material. This would indicate that freeze drying the tissue had little effect on PME activity, and that about 24% of the PME was bound to CW.

5.3.1.2.6. Procedure for potato PME determination.

The procedure finally adopted was:

A sample of 10.0 g freeze-dried potatoes (equivalent to 40 g fresh weight) was extracted with 80 ml 1M NaCl (section 4.3.3.5.1.). An aliquot (4 ml) of 0.6% pectin solution was pipetted into the pH-stat reaction cell, maintained at 30.0±0.1 °C with a water jacket, and the

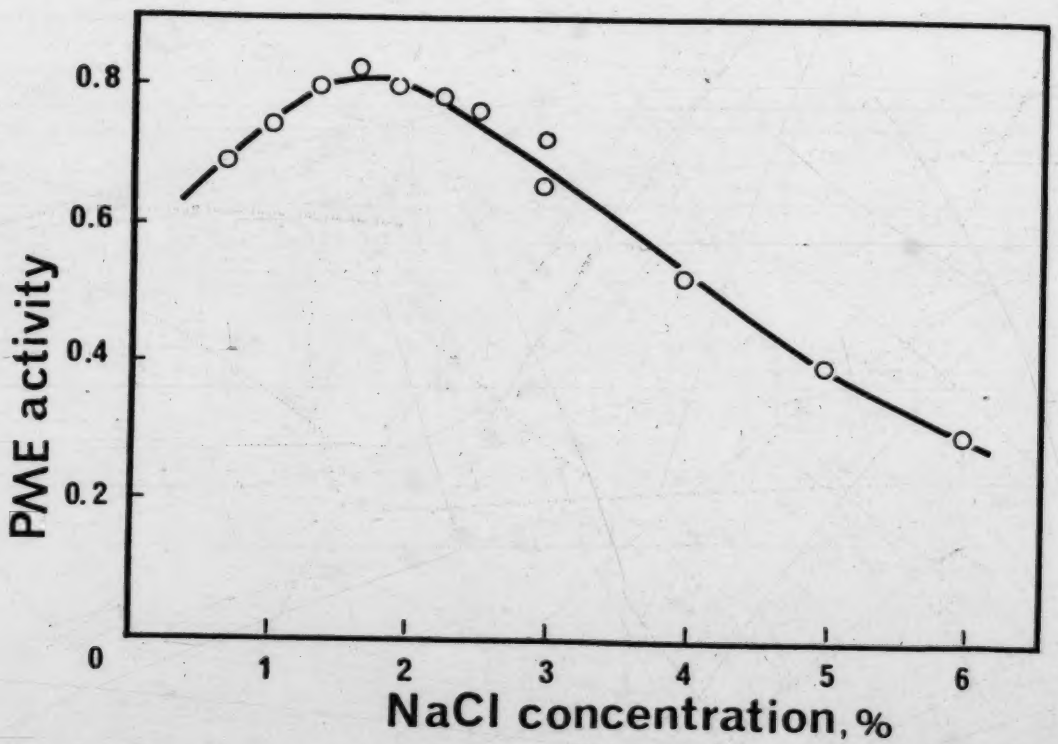


Figure 50. Effect of NaCl concentration in the reaction mixture on PME activity.

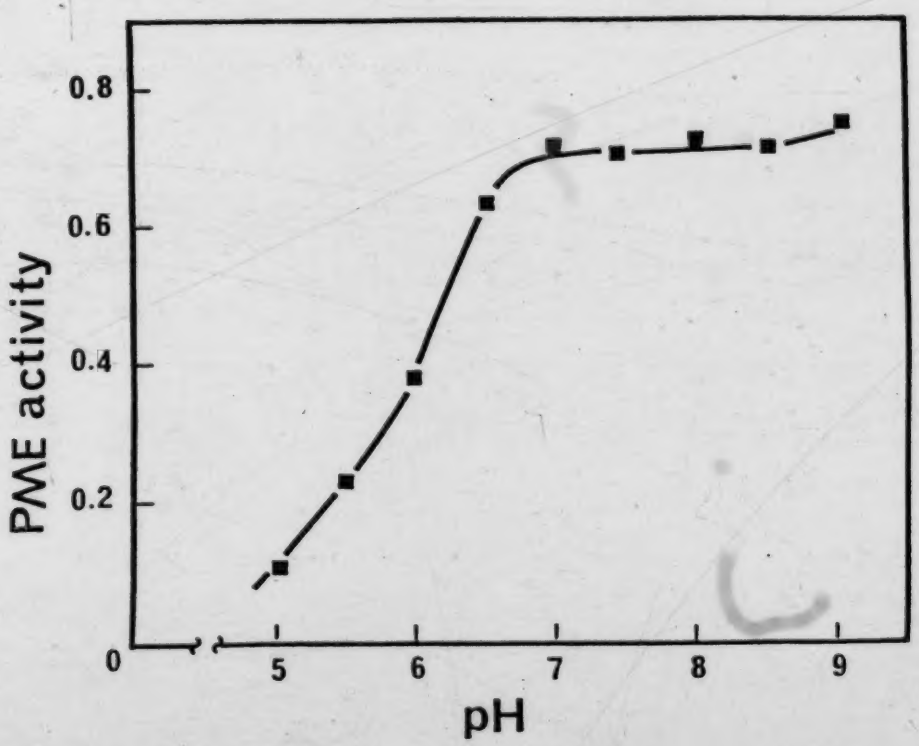


Figure 51. Effect of pH on PME activity.

magnetic stirrer started. After allowing 2 min for the pectin to reach 30°C, 2 ml of enzyme extract were added. The pH of the reaction mixture, now having about a 2% NaCl content, was quickly adjusted to slightly above 7.5 by adding NaOH, and the automatic titrator started. The consumption of 0.01M NaOH as a function of time was recorded for 15-20 min. Enzyme activity per ml of enzyme extract per min was evaluated from the slope of the linear portion of the activity line and converted to PME units (number of carboxyl groups liberated in a min per g of dry matter of tissue) knowing that, stoichiometrically, 1 μM COO^- = 1 ml 1mM NaOH.

5.3.1.3. Effect of SO_2 on PME Activity.

Reducing agents are known to generally inhibit enzyme activity, so it was of interest to determine if the SO_2 added during peeling and slicing stages affected the role of PME during precooking. It was doubtful that the potatoes picked up SO_2 levels as high as those used in this PME study. The presence of up to 1000 ppm SO_2 did not have an inhibitory effect on PME action (Table 9).

Table 9. Effect of SO_2 on PME activity.

ppm SO_2	Enzyme activity*
0	0.78
50	0.82
200	0.79
500	0.79
1000	0.77

*PME units/min/ml of enzyme extract.

Results from PME studies confirmed the observations made by other workers (Bartolome and Hoff, 1972a,b ; Keijbets et al., 1974) that potato PME is quite thermally resistant. As indicated by the release of free carboxyl groups, PME is not active to any appreciable extent until about 50°C. Its activity is maximum at 60°C, and negligible at 70°C and above. Thus, enzyme activation takes place in a temperature region slightly below the onset of thermal inactivation. This is also the region where firming of potato tissue has been observed (Reeve, 1954a,b,c ; Potter et al., 1959 ; Bartolome and Hoff, 1972b), implying that the choice of time and temperature for precooking is very critical.

The above indicated that, at precooking temperatures, the conditions in potato tissue are suitable for enzymic demethylation and metal-bridge formation, as proposed by Bartolome and Hoff (1972b). Noteworthy is the appreciate amount of thermal demethylation at precooking temperatures (Figure 52). This would augment the number of the free carboxyl groups available for formation of salt bridges.

5.3.2. Mineral and Pectin Content of Potato Tuber, its Starch and CW/ML.

The mineral composition of potato tuber, its starch, and CW/ML is shown in Table 10. This analysis was carried out to determine the P and Ca content to enable both the preparation of Ca-starches and the simulation in model studies of the relative proportion of the constituents in the potato tuber. The starch and CW/ML, which constituted about 80% of the dry matter in potato, accounted for about 45% of the total Ca^{2+} in the tissue, compared to 80% reported by Bartolome and Hoff (1972b). These authors used wet ashing with $HClO_4$:HNO_3, a technique which, in the present work, presented difficulties, and gave lower P and Ca values, especially for whole tuber. However, Ca^{2+} contents for both the CW/ML

Table 10. Mineral composition of whole potato tuber and its starch and cell wall*.

Tuber size**	Ash (%)	P	Ca	Mg	Na	K
A	2.68 ± 0.30	156.7	34.8	106.2	33.8	1812
B	4.91 ± 0.13	192.6	42.2	126.8	34.1	1850
C	3.55 ± 0.11	141.3	36.9	123.0	37.9	1871
Average ± $\bar{S}$	3.71 ± 1.12	163.5 ± 26.3	37.9 ± 3.7	118.7 ± 10.9	35.3 ± 2.3	1844 ± 30
			Starch			
A	-	70.6	18.7	18.4	23.8	15.1
B	-	72.3	14.4	15.3	28.2	17.8
C	-	69.1	10.2	18.2	22.3	20.6
Average ± $\bar{S}$	0.36 ± 0.09	70.7 ± 1.6	14.5 ± 4.3	17.3 ± 1.7	24.8 ± 3.1	17.8 ± 2.7
			Cell Wall			
B						
Average ± $\bar{S}$	-	9.3 ± 0.2	124.0 ± 8.7	130.0 ± 4.4	60.0 ± 3.5	121.0 ± 14.5

*In mg per 100 g dry matter (cv. Netted Gem, Southern Alberta).

**A, 110-168 g (4-6 oz), B, 169-224 (6-8), and C, 225-336 (8-12).

and starch were in good agreement with Bartolome and Hoff (1972b).

CW/ML constituted about 5.0±0.1% of the tuber dry weight. This was comparable to the value of 5.6±0.6% reported by Hoff and Castro (1969). Pectin content and its DE value in potato CW/ML are shown in Table 11. The AGA content, as determined by the Cu^{2+} ion-exchange technique (Keijbets and Pilnik, 1974a), and the carbazole reaction method (McComb and McCready, 1952), were comparable. The Cu^{2+} ion-exchange procedure, performed before and after saponification, enabled the calculation of both the DE value and pectin content. The calculation, based on the stoichiometrical reaction of two pectic carboxylic groups with one Cu^{2+} ion, is shown in the Appendix. It should perhaps be noted that the formula given by Keijbets and Pilnik (1974a) is misleading, although their uronide content of 16.3% and DE of 58% are in agreement with the present data.

5.3.3. Effect of Precooking Temperature on DE and Solubilization of Pectin in CW/ML.

Incubating CW/ML in a buffer system at precooking temperature supported the data obtained in the assay of PME. Highest demethylation was obtained at 60°C when the DE decreased from 54.5% to 51.7% (Table 12). Bartolome and Hoff (1972b) reported a decrease in methoxyl content of 5-10%. Taking into account the fact that CW/ML has about 24% of the total PME activity in fresh tubers, a decrease of 2.8% in the DE would represent a decrease of 11.2% in the tuber. Whether metal-bridge formation involving this quantity of galacturonic acid monomer can reasonably be expected to account for the textural changes may be questioned.

The results also indicated that a relatively minor portion of the CW/ML pectin solubilized at precooking temperatures. However, the

Table 11. Degree of esterification (DE) of pectin, and its content of anhydrogalacturonic acid (AGA %) in potato cell wall preparation.

Cell wall preparation*	Cu^{2+}-ion exchange method		HCl-hydrolysis-carbazole method
	DE	AGA, %	AGA, %
I	55.17	16.10	16.17
II	55.13	16.40	16.25
III	54.55	16.28	16.38
IV	54.58	15.87	16.20
Average ± $\bar{S}$	54.91±0.29	16.16±0.23	16.25±0.13

*Preparations had 373±8 µM free-COO^- and 827±17 µM total COO^- groups/g cell wall dry matter.

Table 12. Effect of precooking temperature on the degree of esterification (DE value) and anhydrogalacturonic acid (AGA) content of potato cell wall/middle lamella pectin.

Temperature °C	DE value	% AGA in residual CW/ML	Solubilized AGA(%)	Total pectin (% AGA) d.m.b.*
25	54.55 ± 0	15.92 ± 0	-	15.92
50	53.36 ± 0.25	15.73 ± 0.03	0.67	16.40
55	52.58 ± 0.25	15.45 ± 0.08	0.71	16.16
60	51.71 ± 0.37	15.04 ± 0.04	0.83	15.87
65	53.32 ± 0.57	15.02 ± 0.04	1.23	16.25
70	54.27 ± 0.30	15.20 ± 0.01	0.91	16.11
75	55.13 ± 0.16	15.34 ± 0.04	0.94	16.28
100	55.71 ± 0.09	10.68 ± 0.05	5.62	16.30

* d.m.b. = dry matter basis
cell wall contained 1.24 mg Ca^{2+} per g dry matter.

nature of the remaining pectin was altered in terms of its methoxyl content. It should be noted that, in this particular study, where "native" CW/ML was used, solubilization of pectin was considerably less than in the later studies when H-CW/ML was used. Native CW/ML contained a substantial amount of Ca^{2+}, suggesting that Ca^{2+} within the CW/ML was also involved in the stablization of the pectic galacturonan.

5.3.4. Pectin Changes in CW/ML Induced by Potato Constituents During Precooking, Cooling and Cooking.

The effect of Ca^{2+}, PME and temperature during precooking is shown in Table 13. With no Ca^{2+} added and in the presence of PME, essentially all the pectin was solubilized, whereas, about half was solubilized in the absence of enzyme. Addition of sufficient Ca^{2+} to neutralize the free COO^- groups in the CW/ML reduced pectin solubility from 14% to 1.38% in the presence of PME and from 7.3% to 0.3% in its absence. At the same time, all the added Ca^{2+} was taken up by the CW/ML. This indicated that Ca^{2+} had a great affinity towards binding on the CW/ML, and stablized pectin against thermal degradation. A similar trend was observed at 100°C.

Ca^{2+} levels above stoichiometric equivalence with pectin free COO^- groups (373±7 µeq/g CW/ML dry matter) did not further suppress pectin solubility, although the Ca-uptake by the CW/ML increased. At a Ca^{2+}/COO^- equivalent of 5, the Ca-uptake by the CW/ML was 930±30 µeq Ca^{2+}/g (compared to the 62 µeq initially present in the CW/ML, Table 10). This suggested that CW/ML had a Ca-binding capacity greater than the quantity that would satisfy the free COO^- groups. The nature of these binding sites of Ca^{2+} remain to be clarified. It has been suggested that phytic acid, known to occur in CW of many vegetables, has a great capacity to

Table 13. Potato cell wall/middle lamella pectin solubilization and Ca-uptake as affected by Ca^{2+} and PME during precooking.

Pre-cooking temperature °C	Ca^{2}/COO^{-} equivalents	AGA %		Ca-uptake by CW/ML (µeq/g dry matter)	
		+PME	-PME	+PME	-PME
60	0	14.01	7.31	-	-
	0.5	2.14	1.22	190	183
	1.0	1.38	0.33	360	350
	5.0	0.56	0.29	900	920
65	0	15.39	8.84	-	-
	0.5	1.58	1.21	203	180
	1.0	1.11	0.31	346	296
	5.0	0.42	0.24	996	900
100	0	-	16.15	-	0
	0.5	-	1.62	-	192
	1.0	-	0.49	-	280
	5.0	-	0.36	-	925

bind Ca^{2+}, and may be involved. Accounting for all the Ca-binding sites may not be possible, but it is clear that the free COO^- groups are not the only sites.

Of interest was the finding that, even in the presence of Ca^{2+}, pectin solubility was greater at both the precooking temperatures studied when PME was present (2.14 vs 1.22 at 60°C and 1.58 vs. 1.21 at 65°C), and that the solubility was greater at 60°C than at 65°C. This indicated that PME may enhance pectin solubilization, particularly at precooking temperatures, in the region of its optimal activity. The results suggested that an appreciable amount of pectin was not stabilized by Ca^{2+}, as indicated by the higher % AGA solubilized in the presence of PME at all levels of added Ca^{2+} (Table 13). The net result would be that, if PME was allowed maximum activity during precooking, the firmness of the tissue would be lower than when PME activity was restricted. This was shown by the results obtained when the firmness of potato tissue precooked at different temperatures was measured. (Section 5.3.5.).

Table 14 shows that a similar trend was observed when Ca-starch was used as the source of Ca^{2+}. Pectin solubilization at 70°C was lower than 60°C, indicating that the pectic substances were more stable at 70° than at 60°C. This suggested that at 70°C more Ca^{2+} was available for stabilization of pectin galacturonan. The precooking temperature, whether 60° or 70°C, determines the extent of starch gelatinization and should, therefore, affect the availability of Ca^{2+} for metal-bridge formation and, hence, the extent of tissue firming.

In the final model study, a precooking temperature of 65°C was chosen as a compromise between 60°C, at which PME activity is optimal,

and 70°C, when all starch granules are gelatinized. When the CW/ML and Ca-starch preparations, precooked at 65°C in the presence and in the absence of PME, were cooked at 100°C with or without cooling, almost all the pectic substances were solubilized when using H-starch (Table 15). About 14.5% from a total of 16.3% pectin was solubilized by thermal degradation during cooking, probably by the β-elimination mechanism proposed by Keijbets and Pilnik (1974b). In the presence of PME a further 1.1% pectin was solubilized during precooking, suggesting that pectin demethylated by PME was rendered more susceptible to thermal degradation.

With Ca-starch, the solubility of 15.6% was suppressed to 7.9% and 9.8%. respectively, in the absence and in the presence of PME, when cooling was omitted (Table 15). Since stabilization of Ca-bridges would not be possible at the precooking temperature, it is reasonable to assume that pectin with a decreased DE is more susceptible to thermal degradation. This would explain the 1.9% difference in pectin solubility between the two treatments.

Enzyme treated sample which was cooled had more solubilized pectin (12%) than that which was not cooled (9.8%). the difference of 2.2% may be attributed to the residual PME activity during cooling. In the cooled sample, some of the free COO^- groups, produced during precooking, would be stabilized by Ca^{2+} released from the partially gelatinized starch. However, it appeared that PME continued to demethylate pectin, the structure of which had been weakened by precooking, thereby freeing more COO^- groups. Pectin with a low DE is expected to be more susceptible to depolymerization than pectin of high DE value. Hence, the total pectin solubilized on cooking, following the cooling step, was higher than when cooling was omitted.

Table 14. The effect of Ca-starch during precooking on cell wall pectin solubilization.

Starch-phosphate neutralization with Ca^{2+}, %	Temperature					
	60°		70°		100°	
	AGA %	Relative Sol. %	AGA %	Relative Sol. %	AGA %	Relative Sol. %
H-starch	6.03	100	6.29	100	13.97	100
25	3.36	55.7	2.75	43.7	8.21	58.8
50	2.18	36.6	1.83	29.1	6.64	47.5
75	2.05	34.0	1.58	25.1	3.10	22.2
100	1.62	26.9	1.31	20.8	2.40	17.2

Table 15. The effect of Ca-starch, Mg^{2+} and cooling on CW/ML pectin solubilization after precooking (65°C) and cooking.

H-cell wall + starch	AGA as %/cell wall dry matter			
	Cooling		No cooling	
	+	-	+	-
H-starch	15.65	14.35	15.58	14.62
Ca-starch	12.01	7.96	9.79	7.92
Mg^{2+}		14.35		

In presence (+) and absence (-) of PME.

It is noteworthy that Mg^{2+} had no effect on pectin solubility. In the Mg^{2+} study, although no PME was present, the H-CW/ML had 373 μeq of free COO^- groups per g, which would be available for the Mg^{2+} to form metal bridges and, hence, affect solubility to a certain extent. In the previous experiments, addition of Ca^{2+}, even in the absence of PME, caused a considerable decrease in pectin solubility. This corroborated the finding of Keijbets et al. (1976) that Ca^{2+} but not Mg^{2+} stabilized pectic galacturonan, and disagreed with the data of Bartolome and Hoff (1972b) which implicated both Ca^{2+} and Mg^{2+} in metal-bridge formation with de-esterified galacturonan.

According to Bartolome and Hoff (1972b), precooking brings about enzymatic demethylation, producing additional free COO^- groups. Thermal diffusion of divalent cations develops cross-linkages between galacturonan chains and renders the pectic substances more resistant to thermal degradation. Data from model studies simulating precooking, cooling and cooking suggest that this might be partially true. However, present data show that pectin stabilization by Ca-bridging among the COO^- groups released by PME may be superceded by pectin solubilization enchanced by demethylation during precooking and cooling.

The inference would, therefore, be that PME has a limited, and possibly negative, role in the firming of potato tissue during precooking. In fact, if maximum firmness of the tissue is desired, precooking should be done at temperatures which would deactivate PME. The temperature chosen should be such that starch is completely gelatinized to make available a maximum quantity of Ca^{2+} for pectin stabilization.

5.3.5. Effect of Calcium on Tissue Firming During the Precook Treatment.

Results from the model studies showed that, during precooking, cooling and cooking, availability of the Ca^{2+} bound to starch, together with galacturonan solubilization and demethylation by PME had a profound effect on the overall solubility of potato CW/ML pectins. Hence, the precooking temperature is very critical.

Studies using potato slices were carried out to further clarify the role of Ca^{2+} and PME on tissue firming during precooking. The effects of precooking temperature, cooling, and Ca^{2+} availability during precooking, cooling and cooking on tissue firmness were investigated. The results shown in Table 16 may be summarized as follows:

1. Steam-cooked tissue was slightly firmer than that cooked in water or in 200 ppm Ca^{2+}.

2. Tissue receiving cooling, with or without Ca^{2+} present, between precooking and final cooking was significantly firmer ($p = 0.05$) than the tissue without cooling. The effect was more pronounced if the tissue was precooked and cooked in the presence of Ca^{2+}.

3. If all three steps were done in water, tissue firmness was not significantly affected by either precooking or precooking temperature. However, if all the steps were done in the presence of 200 ppm Ca^{2+}, the firmness of tissue precooked at 70°C (751±47 g) and 75°C (763±20 g) was significantly greater ($p = 0.01$) than that precooked at 65°C (435±26 g).

4. If steaming was used in final cooking, whether the previous two steps were done in the presence or absence of Ca^{2+}, the resultant tissue was significantly firmer ($p = 0.01$) than when water-cooking was used.

Table 16. Effect of precooking temperature, cooling and Ca^{2+} on firmness of cooked potato tissue.

	Tissue firmness (penetration in g-force)
1. Cooked in water	260 ± 24
2. Cooked in 200 ppm Ca^{2+}	263 ± 9
3. Steam-cooked	286 ± 20
4. Precooked(65°C), cooled and cooked in water	246 ± 18
5. As # 4, but precooked at 70°C	296 ± 32
6. As # 4, but precooked at 75°C	278 ± 24
7. Precooked (65°C),cooled and cooked in 200 ppm Ca^{2+}	435 ± 26
8. As # 7, but precooked at 70°C	751 ± 47
9. As # 7, but precooked at 75°C	763 ± 20
10. Precooked (70°C) and cooked in water	266 ± 20
11. Precooked (70°C) and cooked in 200 ppm Ca^{2+}	416 ± 23
12. Precooked (70°C) in water and steam-cooked	334 ± 8
13. Precooked (70°C) in 200 ppm Ca^{2+} and steam-cooked	385 ± 25
14. Precooked (70°C) and cooled in 200 ppm Ca^{2+}, and cooked in water	374 ± 15
15. Precooked (70°C) in 200 ppm Ca^{2+}, cooled in water and cooked in 200 ppm Ca^{2+}	564 ± 24
16. Precooked (70°C) and cooled in 200 ppm Ca^{2+}, and steam-cooked	547 ± 37
17. Precooked (70°C) and cooled in water and steam-cooked	452 ± 21

Therefore, the following inferences may be made:

1. Precooking and cooling are necessary for tissue firming, since cooking alone, even in the presence of Ca^{2+}, does not bring about the desired effect.

2. Ca^{2+} availability is more important than the production of extra COO^- groups by PME. Precooking at the temperature optimal for the enzymatic acticity resulted in tissue that was less firm than that precooked at a temperature at which the enzyme was largely inactivated. At higher temperatures (70° or 75°C) starch was completely gelatinized (Chung, 1979), resulting in a greater release of Ca^{2+}. It would appear, then, that the primary aim of precooking is to gelatinize the starch, rather than to activate PME as proposed by Bartolome and Hoff (1972b).

3. If maximal firmness is desired, e.g., in canned, whole or diced potatoes, additional Ca^{2+} is required in precooking, cooling and cooking steps. However, this may not be the case in the production of potato granules, where overly firm tissue may result in excessive cell rupture during mashing.

4. Cooking in water of low Ca^{2+} content, e.g., soft tap water, may, due to leaching of Ca^{2+}, counteract the benefits of precooking (Haydar et al., 1979). Steam-cooking would minimize this undesirable effect.

In light of the results from the studies of model systems and of intact tissue, the following mechanism is proposed to explain the firming of potato tissue by the precooking and cooling treatment:

Precooking serves primarily to gelatinize starch, a major source of Ca^{2+} in potatoes, rather than to activate PME. It also serves to

loosen the tightly enmeshed structure of pectic substances in the CW/ML, exposing the esterified and free pectic COO^- groups to further demethylation and Ca-bridge formation. The heat also provides the necessary energy of activation for Ca-bridge formation. The Ca^{2+} released from gelatinized starch would, given sufficient time, diffuse to the CW/ML, where it would form Ca-bridges with free COO^- groups present on the pectic galacturonan and those made available by thermal demethylation. Cooling reduces the calcium-pectate solubility, allowing the stabilization of Ca-bridges being formed. Once stabilized, the Ca-bridges would render the pectin galacturonan more resistant to further thermal degradation, as has been proposed by Bartolome and Hoff (1972b) and later corroborated by the results of Keijbets et al. (1976).

Thus, if precooking and cooling steps are omitted, Ca^{2+}, although released from the gelatinized starch, would be unable to form stable Ca-bridges due to the excessive thermal energy during cooking. At the same time, cooking would solubilize most of the pectin present, thus further reducing tissue firming.

Results in section 5.2. implied that pectin stabilization by Ca-bridging could involve the ML as well as the CW. Maximal CW firming is desired to prevent cell rupture. However, the degree of ML pectin solubilization, which determines cell cohesion, must be controlled so as to prevent sloughing during cooking, yet allow easy cell separation during mashing. Clearly, a balance between CW and ML firming is essential. The desired firming may be achieved by controlling temperature, time, and levels of added Ca^{2+} during precooking and cooling.

5.4 FURTHER DEVELOPMENT OF THE F-T PROCESS.

5.4.1. Effect of Product Temperature at Predrying.

According to Ooraikul (1978), the F-T process is considered to have been successfully carried out when the following are obtained:

a. A minimum amount of discard (particles >18 mesh), usually 1-2% or less, to avoid economic loss.

b. A maximum amount of fine granules (<60 mesh), normally not less than 80%, to avoid excessive reprocessing and/or reduction in product quality.

c. A minimum amount of broken cells in the final product, normally 1-3%, to avoid a gluey reconstituted product.

The data in Table 17 indicate that the temperature of the mashed potatoes entering the predrying step is crucial, the optimal range being 8±2°C.

The thawing must be complete before proceeding to predrying, otherwise it is not possible to stir and dry the mash uniformly, due to "case hardening" on the outside of the still frozen lumps. Unnecessary cell damage occurs due to the breaking of the frozen mass and shearing of the soft cells against the rigid ice crystals.

Once thawed, however, the potatoes should be predried immediately to avoid undue raising of temperature which results in reabsorption of the released water back into the cells, as observed by Ooraikul (1973), and Greene et al. (1948). Such a mash behaves like unfrozen product and hence, is difficult to handle and predry due to the formation of case hardened balls which were often as large as 2 cm in diameter.

Thus, extended thawing has several deleterious effects on the F-T process. It allows moisture reabsorption into the cells. This negates the benefits of the freezing step (i.e. toughening of the

Table 17. Effect of product temperature at predrying on the yields of fine granules, discard and broken cells in the final product.

Temperature °C	% Yield (-60 mesh)	% Reject (+18 mesh)	% Broken cells
0	64.2	3.4	8
4	79.7	1.8	5
7	91.8	0.1	2
10	91.4	0.7	2
12	82.4	0.7	3
15	64.6	2.8	5
18	58.6	3.7	7

Table 18. Effect of moisture content at granulation on the yields of fine granules, discard and broken cells in the final product.

% Moisture content	% Yield (-60 mesh)	% Reject (+18 mesh)	% Broken cells
46.5	72.0	0.9	5
44.1	91.4	0.7	3
41.7	91.8	0.1	2
38.9	81.2	0.8	2
36.0	70.0	4.7	5
28.0	43.0	7.7	10

potato cells and diffusion of water from within the cells to the outside) which form the basis of the F-T technique. Also, microbial contamination and growth, as well as undesirable chemical changes, may occur if the thawing is unduly long.

5.4.2. Effect of Moisture Content at Granulation.

It is apparent from Table 18 that the moisture content of potatoes at granulation has a profound effect on the success of the process, and that the critical moisture range is between 40 and 44%. Outside this range the yields of the fine granules were unacceptably low, mainly due to an increase in the intermediate size granules at the lower moisture values, and ball formation at the higher values.

Thus it would seem that, within the critical moisture range, the potato cells are more resistant to shear and compression, enabling a more efficient granulation. Experience in this laboratory shows that, when necessary, it is better to start granulation at the upper rather than the lower end of the critical moisture range as there is a margin for correction. For the A-B process, this critical moisture range has been established to be between 33-35%, when the product is friable and can be handled with minimal mechanical damage to the potato cells (Olson et al., 1953; Potter, 1954; Cooley et al., 1954; Harrington et al., 1959).

5.4.3. Variation of Raw Material.

The experiments showed that the F-T process could handle potatoes with a wide range of dry matter content. Similar yields, with respect to the amount of fine granules and product characteristics, were obtained when potatoes with 19, 22 and 25% dry matter were used. Upon reconstitution with hot water (1:4, v/w), all the granules produced mealy and fluffy potatoes of a firm texture.

Some changes of process parameters had to be made during predrying. The duration of predrying depended on the amount of moisture removed (Table 19). Potatoes of low solids required lower stirring speed and higher air velocity and temperature to minimize undue mechanical damage to the potato cells and to rapidly remove the moisture which would otherwise be reabsorbed, resulting in a soggy mash that could not be predried successfully due to ball formation.

The A-B process, on the other hand, is quite susceptible to variation in the dry matter content of potatoes (Boyle, 1967; Ooraikul, 1978). The processor normally does not accept potatoes with dry matter lower than 20%, since such potatoes give products of inferior textural quality (Harrington et al., 1959; Olson et al., 1953). However, products from very high dry matter potatoes are soggy when the usual ratio of granule to water (1:4, v/w) is used for reconstitution (Tamura and Packer, 1976). A-B granules processed from potatoes of different dry matter contents varied in their consistency when reconstituted, prompting one processer to only accept potatoes with dry matter of 20-22%.

5.4.4. Process Parameters and Stirrer Design.

During the predrying stage, "turning and mixing" of the mash is desirable. A stirrer was designed to optimize this effect. The stirrer designed by Ooraikul (1973) was a rotary type made up of two aluminium arms fitted with 0.32 cm diameter bent brass rods and fixed on to the central drive shaft. This stirrer was used for both predrying and granulation. A fan type of stirrer was designed to maximize turning and mixing of the mash during predrying. The fan consisted of a central body which could easily be fitted to and removed from the drive shaft. Attached to the body on either side were aluminium blades (5 cm thick

Table 19. Predrying parameters for processing potatoes of different dry matter contents.

Potato cultivar	% dry matter	Predrying parameters			% Yield (-60 mesh)	% Reject (+18 mesh)	% Broken cells
		air velocity (m/min)	air temp. (°C)	stirrer speed (rpm)			
Netted Gem (N.A.)*	19	150	65	15	90.0	1.0	3
Norgold	22	140	60	20	91.4	0.7	2
Netted Gem (S.A.)*	25	130	60	30	91.8	0.1	2

*N.A. = Northern Alberta
S.A. = Southern Alberta

and 10 cm long) fixed at a 45° angle such that the mash had to pass over the blades during stirring. The clearance between the stirrer and the fluid bed was 0.2 cm, and that from the side of the fluid bowl was 0.3 cm.

Tests showed the fan type stirrer to be more efficient, as indicated by no "ball" formation, minimal sticking of the product to the fluid bed wall, considerable decrease of intermediate size (between 60 and 18 mesh) product, increase of fine granules ($<$ 60 mesh), and little reject material ($>$18 mesh).

During granulation, a controlled degree of attrition forces is desirable to granulate the product to 60 mesh size without actually breaking the potato cells. Another stirrer was designed to optimize "impact" and "shear" forces (Ooraikul, 1973). The stirrer consisted of the main body with a hole for the drive shaft and 1.5 cm thick aluminium bars, bent to fit the bottom of the fluid bowl. Along the bottom of the bar were fitted eight inverted T-rods to increase the area of contact between the granules and the stirrer. Both the stirrers are illustrated in Figures 10 and 11.

Better turning and mixing exabled lower inlet air temperature, and shorter duration for the predrying stage, and increase in the attrition forces enabled less rigorous granulation. Thus, by manipulation of processing parameters (Table 20), the use of these two separate stirrers at the predrying and granulation stages, seems to indicate a better control and efficiency of the process. Improvements included an increase of the fine ($<$60 mesh) granules from 80-85% to 90-92%, mainly due to a decrease in the intermediate (18-60 mesh) sized granules, decrease in discard particles from up to 3% to about 1%, and decrease in broken cells from 3-5% to 2-3%.

Table 20. Some process parameters for F-T technique.

Process parameter	Predrying 15-18 (20-22) min	Granulation 10 (10) min	Final drying 10-15 (10-15) min
Stirrer speed (rpm)	30 (20)	400 (500)	0 (0)
Air velocity (m/min)	130 (115)	30 (15) for 8 min 50 (50) for 2 min	115 (90)
Air temp (^{o}C)	60-65 (93)	25-32 (52)	72 (85)

Data are for 2.5 kg load.

Figures in parentheses are from Ooraikul (1973)

5.4.5. Semi-continuous Operation of the F-T Process.

In the semi-continuous operation of the F-T process the prime objective was to process the potatoes such that each step was accomplished continuously and that the product was progressively removed and collected for the next processing step.

Thus, during the 20 min predrying stage, the fluidized particles were dried to a moisture content within the critical range of 40-45% and progressively conveyed to the cyclone collector. Air velocity was the most critical processing parameter. It has to be adjusted such that sufficient fluidization of the mash was attained, and, as the product was being separated and dried, particles of 40-45% moisture content were entrained and removed from the fluid bed dryer. The air velocity also determined the termperature of the air that had to be used. Too high air temperatures resulted in case-hardened balls in the mash, whereas too low temperatures allowed the potato cells to reabsorb moisture, resulting in a gluey mash. Neither type of mash could be fluidized.

Successful predrying was achieved when the mash was slowly stirred at 20 rpm with the stirrer designed for that purpose. The air temperature and velocity were, respectively, 65°C and 110 m/min. The predried product in the collector consisted of small agglomerates of a few cells, and was ready for granulation.

During granulation, the air velocity was reduced to 52 m/min, a level that fluidized and suspended the particles in the lower section of the fluid bowl. This ensured maximum contact with the granulation stirrer, which was being stirred at 360 rpm. As the potato agglomerates were being granulated into single potato cells, they were fully suspended

in the air stream and conveyed to the cyclone spearator. This has an added advantage in that the separated cells are passed over to the next stage and, therefore, are not subjected to further mechanical forces. After the 10 min granulation period, the product in the collection jar was essentially individual potato cells. The particles that remained in the fluid bed were unmashed pieces and aggregates of several cells too large to be conveyed, and were normally mixed together with the next batch of potatoes. During continuous processing, the amount of such particles would stabilize at a certain level, and they may have to be removed at regular intervals. For six complete runs, the oversize and, therefore, reject material amounted to 1.5% of the total dried product.

During the final drying step, lasting about 10 min, the velocity of the air was further reduced to 40 m/min, and its temperature was increased to 70°C. The stirrer, normally not used during drying in the batch process, was set at a speed of 10 rpm to slowly sweep the particles over the perforated bed and, therefore, enhance fluidization. As the potato granules were being dried, they became suspended in the air stream, where further dehydration took place to the point that they were finally carried away to the cyclone separator. Under these conditions the moisture content of the final product was within the desired range of 6-7%.

A sieve analysis of six batches of the dried product showed that the yield of fine granules (<60 mesh) was 90±4%. Intermediate size particles (between 60 and 35 mesh) constituted the remaining 10%, and could be mixed into the thawed mash to be processed without having any deleterious effect. The percent broken cells never exceeded 2-3%. The

processing parameters for the three stages of the operation are shown in Table 21.

The results obtained in this experiment would be valuable in designing a continuous F-T processing line. A continuous unit covering the three major steps of the process may be designed such that three units of differently modified fluid bed dryers are connected in series, as shown in Figure 53.

The first unit is a predryer into which the thawed mash is continuously fed through a hopper and screw mechanism and the product which is collected in the first cyclone collector. The predried particles are then fed through a screw conveyor into the granulator, where they are granulated with a high speed stirrer under low air velocity. The granulated particles are continuously collected and fed into the suitably designed dryer. Each of these three units is connected to separate control mechanisms to individually regulate the processing parameters, i.e., air velocity, and temperature, and stirrer speed.

It would also appear that some energy savings are possible with these proposed units. For example, the exhaust air from the drying unit may be recycled, with or without reheating, to the predryer. The exhaust from the predryer may be further recycled to the thawing unit, where the frozen mash is thawed to about 5-8°C, and the cool exhaust air from this unit can be reused to precool the hot mash prior to freezing.

Table 21. Processing parameters for semi-continuous operation of the F-T process.

Parameter	Predrying	Granulation	Drying
Time (min)	18-20	10-12	8-12
Stirrer speed (rpm)	20-30	360-400	10-15
Temperature (^{o}C)	60-65	25-30	65-70
Air velocity (m/min)	100-110	50-52	35-40
Moisture content (%)	40-45	38-40	6-7

Data average of 6 runs using 2.0 kg initial load.

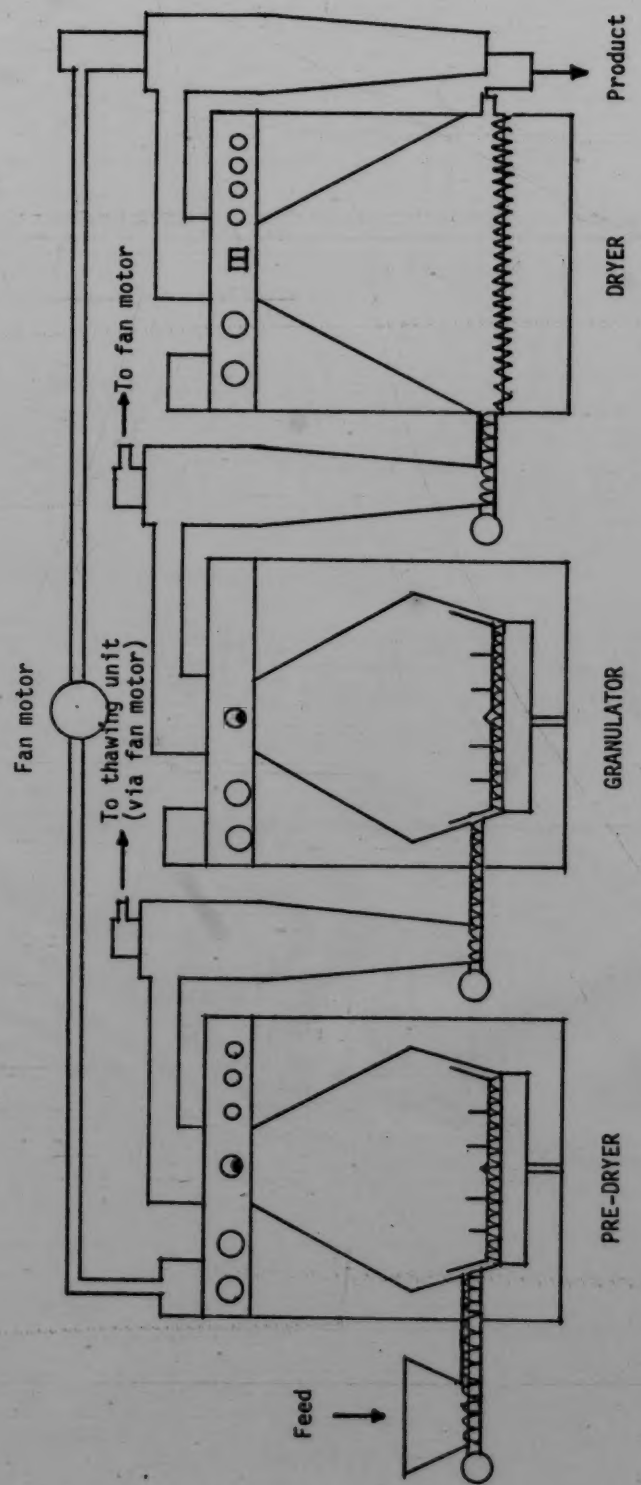


Figure 53. An outline for the proposed continuous F-T process unit.

5.5. PHYSICOCHEMICAL CHANGES DURING AGING OF POTATO GRANULES.

5.5.1. Water Holding Capacity (WHC).

The effect of aging on the WHC of A-B and F-T granules is shown in Figure 54. The initial WHC of fresh F-T granules, ranging from 354-373% (g water per 100 g dry matter), remained unchanged until the 20th week of storage, then increased dramatically to a maximum of 478% at 52 weeks. The WHC of fresh A-B granules increased quite rapidly from 348% to 441% within 4 weeks of storage and then gradually to a maximum of 530% at 49 weeks. In both types of granules a decrease in the WHC was noted during prolonged storage.

5.5.2. Swelling Power (Cold Water Swell, CWS).

Figure 55 shows the CWS of A-B and F-T granules. The CWS for both types of granules decreased from about 37 ml to a minimum of about 27 ml (A-B) and 31 ml (F-T) after 40 weeks of storage, then it gradually increased. Physicochemical changes in granule constituents during the 40 weeks storage caused the insoluble residue to form a more dense pellet in the centrifuge tubes when CWS was determined. The data also indicated that WHC, with an opposite trend of change during storage, was a measurement of mainly "free" water not water "bound" molecularly by the granules.

5.5.3. Degree of Retrogradation.

Results in Table 22 show that starch, a major compenent of the granules, gradually lost its solubility (a measurement of retrogradation) during 30-40 weeks of storage. The solubilities of starch from A-B and F-T granules decreased to 52% and 34%, respectively, of their original values. On further storage a reversal of retrogradation was observed.

Gelatinized starch is known to retrograde (Hodge and Osman, 1976). Potter (1954), working with model systems of potato starch gels,

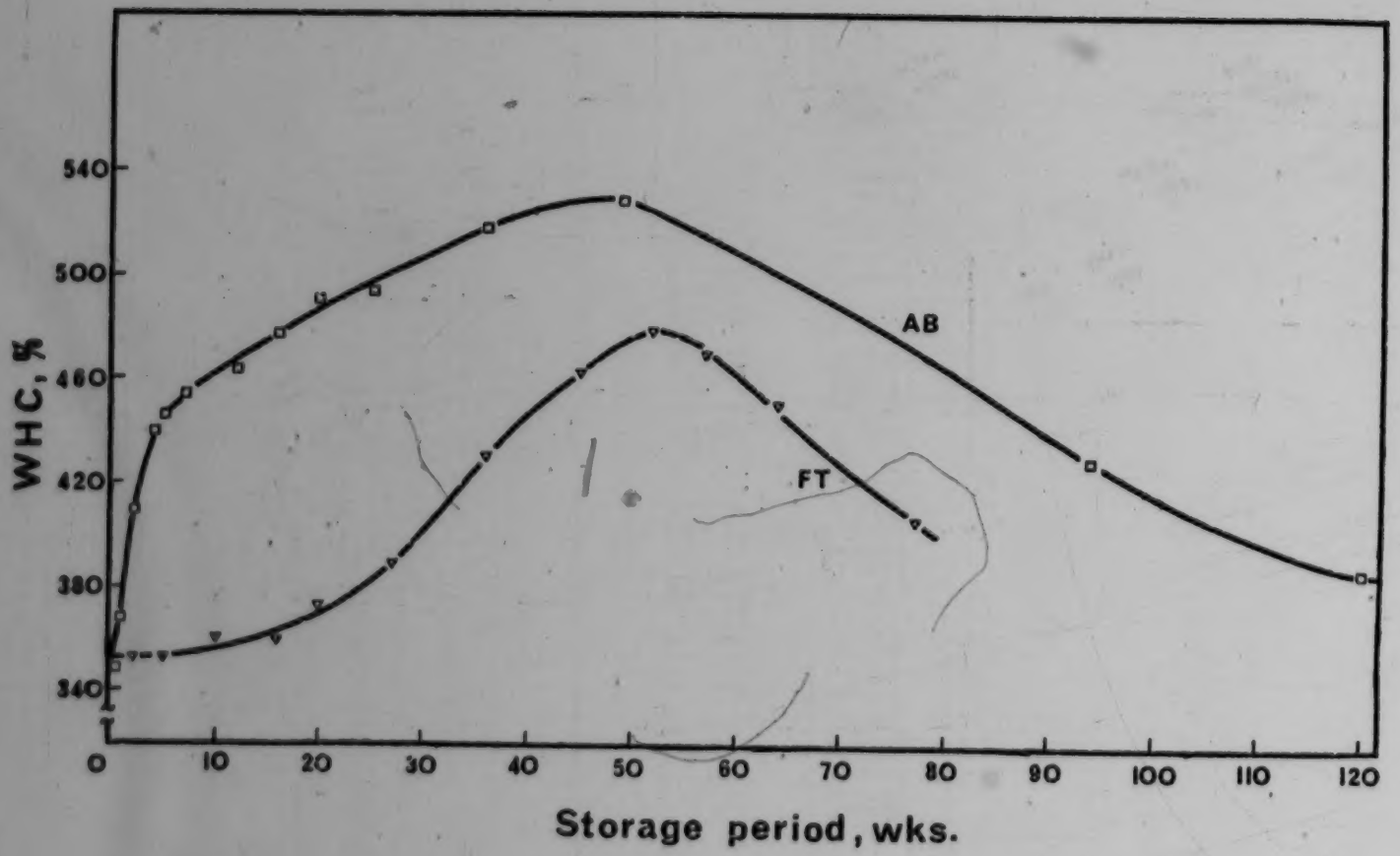


Figure 54. Effect of aging on the water holding capacity of A-B and F-T granules.

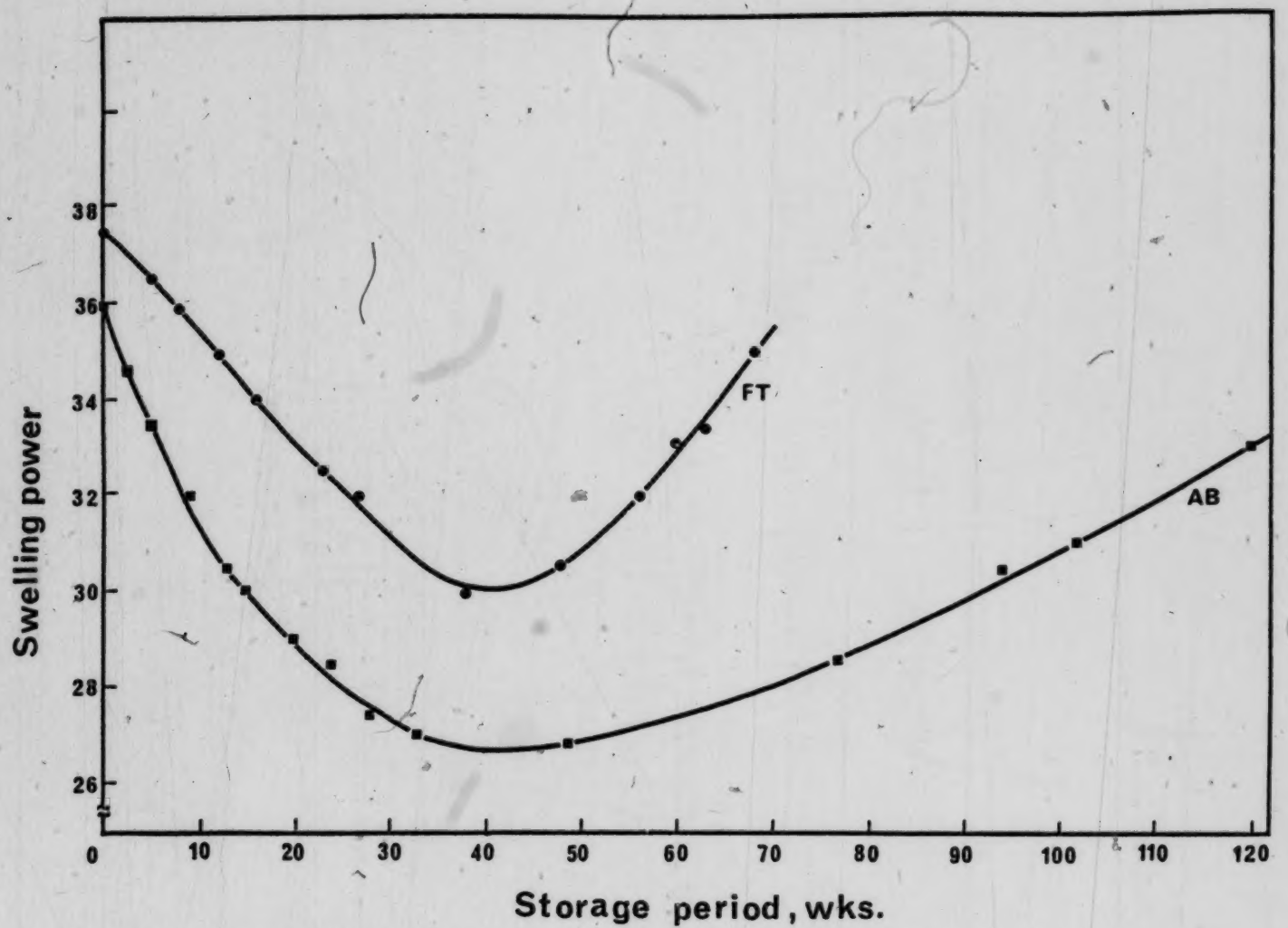


Figure 55. Effect of aging on the swelling power of A-B and F-T granules.

Table 22. Retrogradation changes in A-B and F-T granules during storage.

Storage period (weeks)	Degree of retrogradation					
	A-B granules			F-T granules		
	BIV*	relative** deg. of ret. (a)	(b)	BIV*	relative** deg. of ret. (a)	(b)
0	166.7 ± 4.6	100.0	68.1	46.1 ± 9.2	100.0	91.2
16	161.0 ± 4.2	96.6	69.2	36.8 ± 2.4	80.0	92.3
36	86.8 ± 4.9	52.1	83.4	15.6 ± 1.1	33.9	97.0
64	-	-	-	30.9 ± 1.9	67.1	94.1
106	222.7 ± 9.9	133.3	57.4	-	-	

BIVs for mashed potatoes before processing were:

1. Mashed potatoes at room temp. (no surfactant) 522.3 ± 18.9
2. Mashed potatoed at room temp. (0.25% myvatex) 362.3 ± 11.6
3. Product 1 after freezing and thawing 268.5 ± 16.3
4. Product 2 after freezing and thawing 107.4 ± 6.3

*BIV = Blue Iodine Value: Aborbance units at 605 nm per g dry matter.

**Relative degree of retrgradation:

(a). Expressed as % of 0 week value

(b). Expressed as $\frac{\text{maximum solubility - sample solubility}}{\text{maximum solubility}} \times 100\%$

e.g., for A-B 0 week granules, $\frac{522.3 - 166.7}{522.3} \times 100 = 68.1\%$

reported that moisture content plays an important role in retrogradation. He found no measureable change in the solubility of starch at moisture contents below 15%. The interdependence of starch retrogradation and moisture was also demonstrated by Hellman et al. (1954). French (1950, however, suggested that starch retrogradation can take place even in the solid state. When the solubility of starch was used as a measure of its retrogradation, the results of the present study showed that starch could retrograde even at the low moisture content of about 7% in potato granules.

5.5.4. Moisture Content.

Changes in moisture contents during storage of A-B and F-T granules, packed in moisture-impervious polyethylene bags, are shown in Table 23. The moisture content (%) increased during the initial 33 weeks of storage from 7.05 and 6.32 to 7.83 and 6.73, respectively, for the A-B and F-T granules, and then decreased, approaching the original values. This suggested that physicochemical changes, such as starch retrogradation, caused part of the "bound" water to be released. This released "bound" water was detected as an increase in the moisture content of the granules during 33 weeks of storage. The trend of the decrease in granule moisture on further storage appeared to be the reverse of that for retrogradation. At this stage the released moisture might have been partly reabsorbed by the molecules of granule components, perhaps in a manner similar to the refreshening of stale bread by heating. However, the exact mechanism might differ.

5.5.5. Reconstitution Times.

For the production of extruded French fries, granules aged for 5-6 months had a reconstitution time of 19 sec which was the most

Table 23. Changes in moisture content of A-B and F-T granules during storage.

Storage period (weeks)	moisture content (%)	
	A-B granules	F-T granules
0	7.05 ± 0.05	6.32 ± 0.04
16	7.64 ± 0.05	6.55 ± 0.03
33	7.83 ± 0.03	6.73 ± 0.03
77	-	5.57 ± 0.01
103	7.16 ± 0.05	-

satisfactory cold-water absorption rate as measured by the present method.

The reconstitution times of A-B and F-T granules, shown in Figure 56, increased with aging to a maximum of about 36 weeks, then decreased. The granules aged for about 6 months had a reconstitution time of 18-19 sec, and formed a dough of satisfactory handling and extrusion properties. However, such granules, especially the A-B type, presented a rancidity problem. Changes in reconstitution times appeared to follow the trend of starch retrogradation. Retrograded starch loses its swelling power and water absorption capacity, causing the reconstitution time of the granules to increase.

5.5.6. Extruder Thrust.

Figures 57 and 58 show that the force required to extrude A-B and F-T French fry dough through the F.I.R.A./N.I.R.D. extruder increased rapidly from 0.75 kg to 1.15 kg, and from 1.25 kg to 2.45 kg, respectively, after 16 weeks of storage. After the maximum was attained, the force required dropped sharply to about 0.7 kg after 25 weeks for A-B granules. and 36 weeks for F-T granules. Further storage of the granules had little effect on the extruder thrust.

The extruder thrust reflects firmness and plasticity of dough. If the dough is dry or floury, as were doughs made from granules less than 20 weeks old, the force required is high and the extruded product tend to break easily and to have ragged edges. Doughs made from granules more than 20 weeks old had a slightly moist appearance and required less force for extrusion into a firm but smooth, continuous string than the doughs made from fresh granules.

The changes in physicochemical properties of potato granules appeared to be closely interrelated. Results from this study indicated

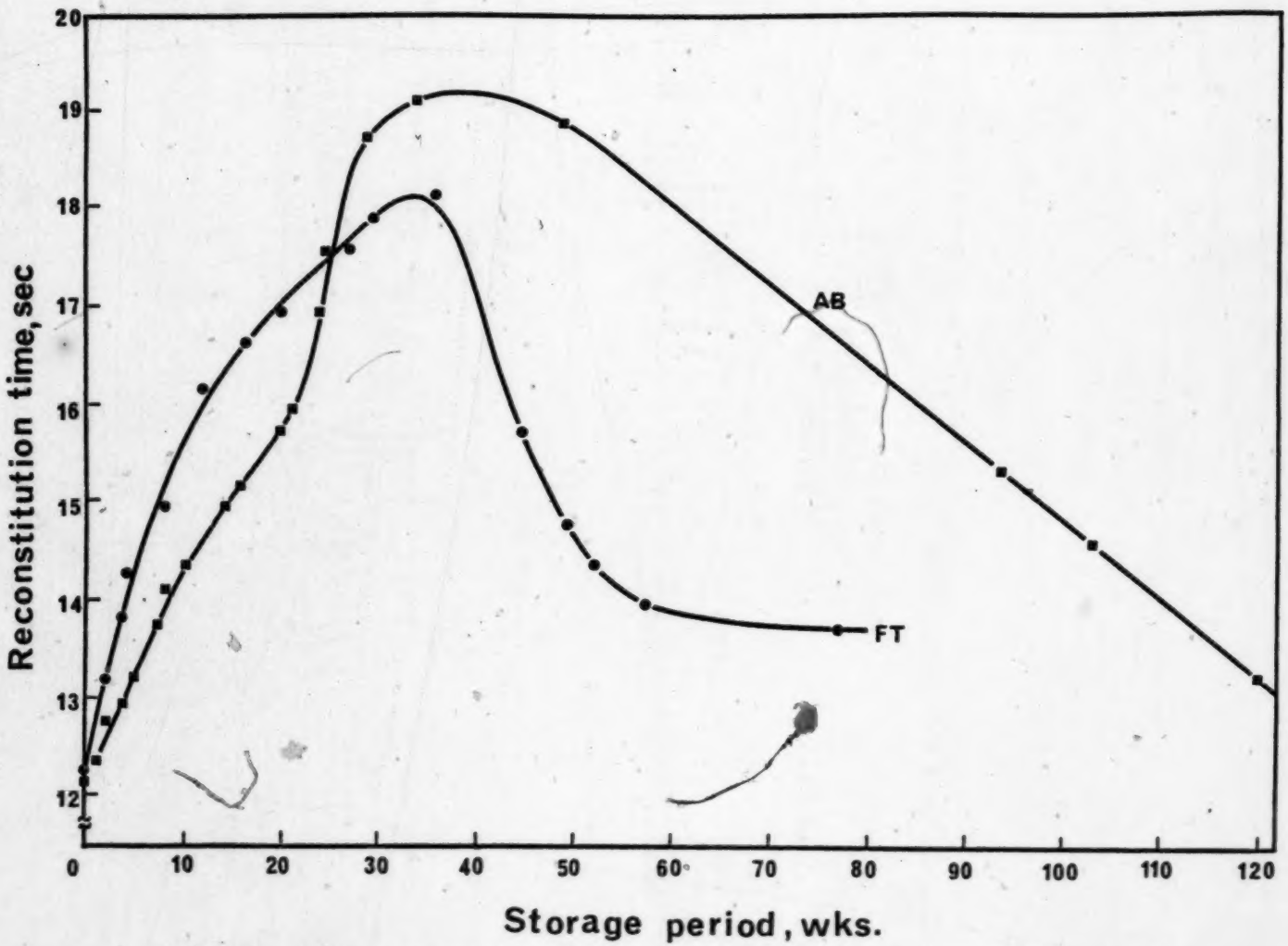


Figure 56. Effect of aging on the reconstitution time of A-B and F-T granules.

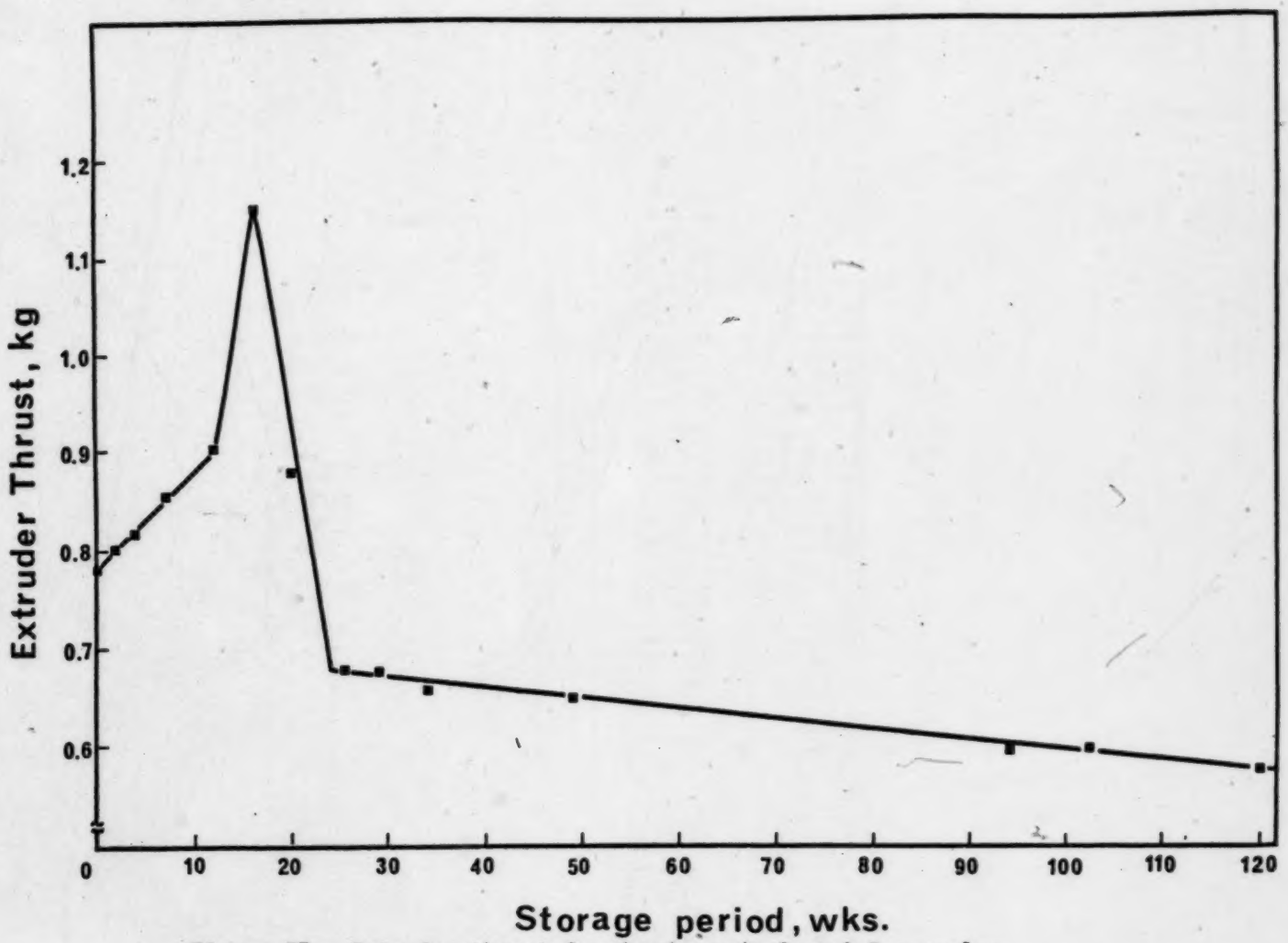


Figure 57. Extruder thrust for doughs made from A-B granules stored for different periods.

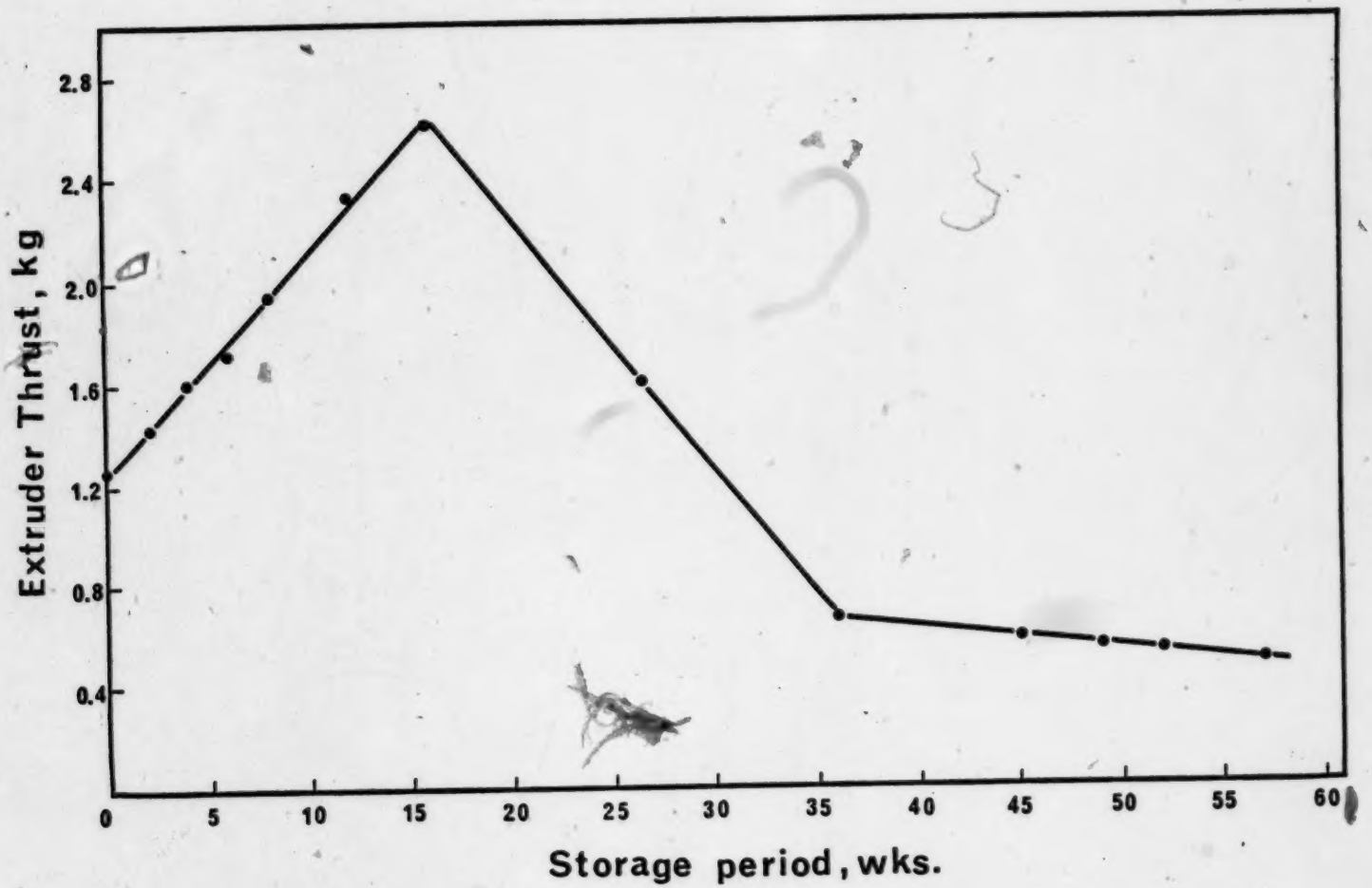


Figure 58. Extruder thrust for doughs made from F-T granules stored for different periods.

that among the properties studied, retrogradation of starch during storage was the primary change that affected other properties of the granules. For example. molecular alignment of starch during retrogradation might have caused the release of part of its "bound" water. This release was detected as a slight increase in moisture content of the granules during storage. The retrograded starch lost its solubility, resulting in a decrease in the CWS of the granules. The alignment of the starch molecules might also have created minute voids in the solid matrix which would trap a quantity of water on reconstitution, contributing to the increase in WHC. The loss of solubility and CWS of starch, therefore, caused the increase in reconstitution time, allowing the granules to absorb cold water uniformly. The increase in WHC and uniform constitution of the granules, in turn, resulted in a reduction in the force needed to extrude the dough.

The change in the degree of retrogradation, itself, is of prime interest. Potato starch consists of 17-21% amylose (Chung, 1979), part of which may, during processing, leach out to the CW or even out of the cell through primary wall pits (Reeve, 1954a). Hence the major fraction of starch remaining inside the granules is amylopectin. Retrogradation is a phenomenon associated mainly with amylose, where linear chains align themselves to form crystalloid regions (Hodge and Osman, 1976). These regions become hydrophobic as "bound" water is replaced by intermolecular bonds of carbon-bound hydroxyl groups. It is possible that amylose, leached out to the surface of the granules during processing, formed crystalloid regions on the CWs during storage, thus inhibiting easy passage of water into the granules during reconstitution, and contributing to the increase in reconstitution time.

Amylopectin may also be involved in retrogradation if its branched chains become sufficiently entangled to form a gel network. However, bonding among the branches of these molecules is much less extensive than those of amylose. For that reason the retrogradation of amylopectin was found to be reversible by mechanisms such as heating, as in the refreshening of stale bread (French, 1950; Hellman et al., 1954). This may partially account for the reverse trend of retrogradation of granules (as measured by starch solubility) on prolonged storage. Retrogradation of amylose, on the other hand, is irreversible (Hodge and Osman, 1976).

Another point of interest is the affect of anions on the swelling power of starch gel. Salt crystals which were observed on the surface of fresh granules (see section 5.1.) could be KCl (Fedec et al., 1977), as K is a major mineral in potato ash. These salt crystals disappeared on prolonged storage of granules (Figure 59). Haydar et al. (1979) found that K^+ favours an increase in viscosity and swelling power of potato starch gel. Possibly the salt absorbed the moisture released from the starch matrix on retrogradation, and dissolved and diffused into the granules. K^+ would, then, bind with orthophosphate groups which were found esterified to hydroxyl groups of amylopectin (Hodge and Osman, 1976). The binding of K^+ on amylopectin resulted in an increase in swelling power and an apparent reduction of moisture content of the granules on prolonged storage.

It is, therefore, quite clear that to achieve an increase in the reconstitution time of potato granules, modification of physicochemical properties of their starch fraction is of utmost importance. This may be accomplished either by aging, which is undesirable due to flavour problems, or by addition of starch modifying agents, such as Ca^{2+}, during processing (Haydar et al., 1979).

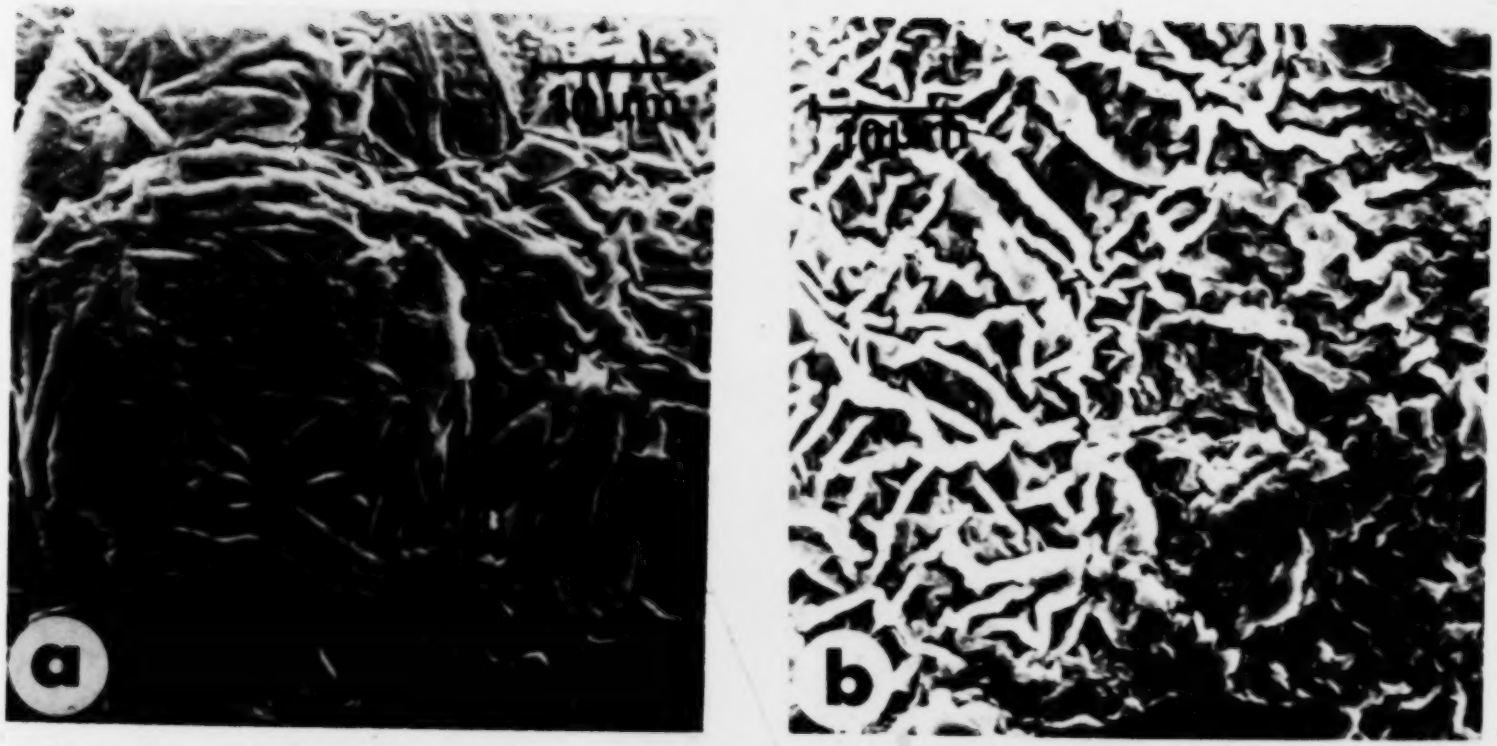


Figure 59. Photomicrograph of "aged" A-B (a) and F-T (b) granule surface showing that the crystals are no longer present.

5.6. AN IMPROVED PROCESS FOR EXTRUDED FRENCH FRY PRODUCTION

5.6.1. Optimum Granule to Water Ratio.

This study indicated that the dry mix-to-water ratio of 1:2 (w/v) recommended by some manufacturers was inadequate. The dough formed was too dry, crumbly, and difficult to extrude, resulting in ragged fries with unacceptable eating quality because of poor texture and oiliness. A similar problem was encountered by Jericevic and LeMaguer (1975) who recommended that the existing ratio of 1:2 for making French fry dough should be corrected. Jadhav et al. (1976) found that a ratio of 1:2.6 was superior for reconstitution and extrusion of extruded fries made from F-T granules.

Preliminary trails indicated that the ratio of 1:2.6 of granule to water was too high. The extruded strips lacked strength, tended to stick to each other and to the fry basket, and in large scale production could not withstand handling between extrusion and frying. The present study indicated that a ratio of 1:2.3 was more suitable as it gave a dough that was uniform, cohesive, and could easily be extruded into appealing strips. The formed pieces could be handled better, and did not stick to each other or disintegrate during frying.

5.6.2. Dough Preparation with the Automash Machine.

Presently, the dough for extruded fries is prepared commercially by pouring a 6 lb can of the mix into a narrow cylinder containing a volume of water twice the weight of the mix, and stirring briskly with a wire wisk. Under such conditions, the granules first contacting the water are converted to a thickened mass, thereby preventing an even distribution of moisture. The resulting dry and wet spots in the dough prevent it from being extruded properly.

An automatic dispensing apparatus was used for reconstituting the dry mix into a uniform dough. The apparatus has a mechanism for simultaneously metering precise amounts of dry mix and cold water into a mixing chamber with thorough blending to form a homogeneous slurry that flows by gravity into the extrusion cylinder. The slurry, after a short period of standing, sets to form a uniform dough, effectively eliminating the problem of wet and dry spots.

5.6.3. Taste panel Evaluations.

In preliminary sensory evaluation of extruded French fries, their characteristics were compared to those of par-fries. A factorial analysis of variance of the results from the first three sessions in series I showed that the difference among judges was highly significant. These results may imply not only that samples differ from one another in their characteristics, but that the judges also differ greatly in their personal perception of French fry quality. Discussion with the panelists at the end of four sessions confirmed the above interpretations and brought out two major points:

(i) Extruded products FT I 2 and AB I 2, although more oily than products FT I 1 and AB I 1, were more crunchy and appealing to four of the eight panelists, who scored these products higher as did the other four panelists. However, the latter considered oiliness a more important factor and, hence, gave a lower score for the overall acceptance of products FT I 2 and AB I 2. Thus, for both the F-T and A-B granule based formulae, although there was no statistical difference between the more oily and less oily products, the A-B fries were rated lower due to their higher oil absorption.

(ii) Four panelists regarded the texture and flavour of the outside skin very desirable and more important than the inner core. They also considered a relatively soft core desirable, since it literally melts and mixes with the crunchy skin, producing a pleasant sensation different from the mouthfeel of conventional fries. The other four panelists considered the inner core of the extruded products too soft.

It appeared that the inner core of extruded fries needed to be somewhat more firm. Also, extruded French fries possessed unique characteristics of their own and should not be compared to ordinary French fries. The first three sessions, therefore, served an important purpose in familiarizing panelists with the range of sensory qualities to be judged.

This acquired familiarity was clearly shown in the fourth session when there was no significant difference among the judges. The interaction between samples and judges was significant ($p=0.05$), while that between samples was highly significant ($p=0.01$). This was taken as an indication that the judges had acquired sufficient knowledge during the first three "training" sessions to competently assess the sensory quality of extruded French fries.

The application of Duncan's Test to the data from the fourth session (Table 24) showed that, at the 5% level of significance, the extruded products were similar in their acceptance and that as a group their acceptance (mean score: 6.1 for A-B products, 6.5 for F-T products) was lower than that of the par-fried potatoes (mean score: 7.4). There was no significant difference in the scores for colour, appearance and outside skin of the five products. However, the scores for the inner core of par-fries were significantly better than those of extruded fries.

Table 24. Duncan's Test of panelists' scores, and yield, moisture and oil contents of the products evaluated in Series I.

Attribute/Composition	Mean scores of the products				
	FT I 1	FT I 2	AB I 1	AB I 2	Par-fries
Colour and appearance	6.4	6.4	7.2	7.0	7.2
Outside skin	7.4	7.0	7.0	6.8	6.9
Inner core	6.4	6.0	5.6	5.4	7.5
Overall acceptance	6.5	6.5	6.2	6.0	7.4
Yield*	2.6 ± 0.1	2.6 ± 0.1	2.6 ± 0.0	2.5 ± 0.1	2.5 ± 0.1
Moisture (%)	52.8 ± 0.3	49.6 ± 0.9	48.2 ± 0.6	44.4 ± 0.2	51.6 ± 0.2
Oil (%)	11.5 ± 0.7	12.8 ± 0.1	13.3 ± 0.6	16.5 ± 0.7	9.7 ± 0.1

*Weight of fries from unit weight of the dry mix.

In a Duncan's Test a line typed under any sequence of means indicates that there is no significant difference at the given percent level (5%).

This was to be expected, as recombined products were being compared with fries made from intact potatoes. However, the F-T products obtained significantly (p-0.05) better scores for the inner core (6.2) than the A-B products (5.5). Formula FT I 1 was selected for further development, since it had the highest acceptance amongst the extruded fries and had the lowest oil uptake (Table 24).

As a result of information obtained in the first series of evaluations, further efforts were concentrated on improving the outside skin and inner core of the extruded fries using formula FT I 1 as the base. Since the product being developed was different from conventional French fries and was not intended to replace the latter, comparison between extruded French fries and par-fries was irrelevant. Hence, further comparisons were made with the "Chipper" mix, since it was the only available product similar to the F-T mixes. To improve the firmness of the inner core, the levels of the two starch components, Textaid and Crisp film, were increased in formula FT II 2 and then compared to formula FT I 1 (Table 2).

Duncan's Test (Table 25) results of the products evaluated in Series II were similar to those for the extruded products in Series I. However, products from the formulae under test were judged better than the "Chipper" product with respect to inner core and overall acceptance. Two important observations were made. When comparing the evaluations of the base formula in the first series with the second series, the mean scores for the inner core and acceptance increased respectively from 6.4 to 6.8 and from 6.5 to 7.0, respectively (Tables 24 and 25). This may imply that the lower scores for extruded products in the first series of evaluations were due to biases of the panelists', who may

Table 25. Duncan's Test of panelists' scores, and yield, moisture and oil contents of the products evaluated in series II.

Attribute/composition	Mean scores of the products		
	FT II 1	FT II 2	"Chipper"
Colour and appearance	6.9	6.8	6.9
Outside skin	7.2	7.3	6.9
Inner core	6.8	6.6	6.0
Overall acceptance	7.0	7.0	6.3
Yield*	2.6 ± 0.1	2.6 ± 0.1	2.5 ± 0.1
Moisture (%)	52.8 ± 0.3	53.6 ± 0.5	41.4 ± 0.2
Oil (%)	11.5 ± 0.7	10.3 ± 0.6	21.9 ± 0.5

*Weight of fries from unit weight of the dry mix.

In a Duncan's Test a line typed under any sequence of means indicates that there is no significant difference at the given percent level (5%).

have had preconcieved expectations of the quality attributes of French fried products. Without the par-fries, the biases of the panelists' was minimized and the scores were more representative of product quality. The biases of the judges were also observed during the first series of evaluations where par-fries, having uneven colour and size in comparison to the uniform colour and size of the extruded products, were scored higher. The above information justifies the view that extruded fries possess their own sensory characteristics and should be considered as a distinct product rather than as a substitute for conventional fries.

Secondly, the inner core and acceptance scores for both F-T products evaluated in Series II were essentially the same, indicating that higher levels of Textaid and Crisp film did not further improve the firmness of the product, although oil uptake was reduced from 11.5% to 10.3%, and moisture retention was increased from 52.8% to 53.6%. A higher amount of starch component would retain more moisture in the fries, reducing oil uptake by a corresponding value. Although no statistical difference was shown, in the author's opinion, product FT II 2 had an inner core (resembling a thick and gummy starch gel) which formed a ball in the mouth and was difficult to swallow. This was considered to be detrimental to product quality. Moreover, higher levels of the additives would increase the cost of the French fry mix.

Correlations of the three attributes considered in evaluating the acceptance of extruded products (colour and appearance; texture and flavour of outside skin; texture and flavour of inner core), showed high relationships with acceptability of the products. The correlation coefficients between acceptance, and colour and appearance, outside skin,

and inner core were 0.35, 0.61 and 0.83, respectively, all being significant at the 1% probability level. Multiple regression analysis indicated that scores for these three attributes accounted for 82% of their relationship with the overall acceptance of the products. The inner core appeared to be the most important factor, contributing about 60% of the correlation, while the outside skin contributed about 30%, and the remaining 10% was ascribed to the colour and appearance.

In the author's opinion, product FT II 2 had a "starchy" and "gummy" mouthfeel and, even after a period of chewing, the inner core did not blend with the outside skin. On the other hand, the core and the skin of product FT II 1 quickly blended together on chewing, producing a unique and pleasant sensation, a desirable characteristic for extruded fries. Based on the above and the fact that higher levels of starch binders did not improve the acceptance of the product, formula FT II 1 was chosen to be the most promising for further development. Using it as the base, Supro 630, a soya protein isolate, was added at a level of 5% (Table 3). The base and fortified products were then compared.

A paired T-test and a Duncan's Test of the panelists' scores showed that there was no significant difference between the products (Table 26). Hence, fortification with Supro 630 did not change the organoleptic properties of the product, but did, though at an increased cost, augment the protein content and, thus, may make extruded French fries more appealing to the consumer. Furthermore, addition of Supro 630 increased the moisture retention from 52.8% to 54.7% and reduced oil content from 11.5% to 9.8% (Table 27). These two factors represent a considerable saving and, thus, may offset the cost of fortification.

Table 26. Duncan's Test and T-test of panelists' scores of products evaluated in Series III.

	Duncan's Test mean scores		Paired T-test	
	FT 1	FT 2	DF	t
Colour and appearance	8.0	7.4	7	0.79
Outside skin	7.7	7.6	7	0.11
Inner core	7.1	6.8	7	0.36
Overall acceptance	7.3	7.1	7	0.27

In a Duncan's test a line typed under any sequence of means indicates that there is no significant difference at the given percent level (5%).

In a T-test t values smaller than theoretical value indicates that there is no significant difference at the given percent level ($t_{0.05} = 3.5$; $t_{0.01} = 3.0$).

Table 27. Yield, moisture and oil content of products evaluated in series III.

	FT 1 Fortified	FT 2 Non-fortified
Yield*	2.7	2.6
Moisture (%)	54.7 ± 0.1	52.8 ± 0.3
Oil (%)	9.8 ± 0.3	11.5 ± 0.7

*Weight of fries from unit weight of the dry mix.

5.6.4. Additives.

The product developed by Jadhav et al. (1976) could not be successfully made during the present investigation. When made on a large scale, the dough was not cohesive enough. The formed pieces of the dough lacked strength and, thus, could not withstand handling similar to that likely to exist in a fast-food outlet. The extruded strips tended to stick to the fry basket and to each other, and disintegrated during frying. The core of the fries was oily, and soft and gummy in texture, and the skin was tough and leathery.

The problems of disintegration during frying, oiliness, soggy skin, and soft and gummy inner core of the extruded product were minimized through proper formulation, suggesting that the composition and properties of additives used in the mix are very critical for the production of good quality extruded French fries. Several formulae were developed to produce extruded French fries with improved texture and eating quality, and freedom from excessive oiliness (Tables 1 and 2). The most successful formulation was the one in which a soya protein isolate was added at a level of 5% to F-T granules (Table 3).

The use of these additives offered several advantages in the processing of fries. Because a linear polymer has a better film and fibre strength than a branched polymer, the use of high amylose starches of the Crisp film type have been recommended in both supported coatings and unsupported films of certain foods (Hullinger et al., 1973). Cremer (1978) found that amylose starch, if it is to be an effective French fry binder, should contain at least 35% amylose. The amylose component, when heated with water in the dough during frying, gelatinizes and retrogrades to form a film (Glicksman, 1969; Ziemba, 1965). The film retards

undue oil penetration and imparts a crisp and crunchy coating with a golden-brown colour to the fried product (Cremer, 1978). In addition, the amylose component adds strength to the product during and after frying, minimizing disintegration.

The amylose starch component has to be complemented by other starch additives ("synergism") in order to maximize its benefits in extruded French fries (Hullinger et al., 1973; Cremer, 1978). Textaid, a cold-water dispersible, cross-linked pregelatinized corn starch, was found to be particularly useful in developing a solid texture and in imparting mechanical strength to the formed pieces so that they could be handled with less breakage between formation and frying.

OK Ceri Gel and OK Pre Jel are simple pregelatinized starches and, hence, have the ability to paste, thicken and gelatinize in cold liquids without the need for subsequent heating (Glicksman, 1969). These additives were used to modify the texture of the product and to improve extrusion properties. Pregelatinized starches also improve stability of dry-mixes by preferentially absorbing moisture.

Baka Snak, the fourth complementary additive used in the mix, is a cold-water dispersible starch derivative which regulates hydration of dry mixes and functions as a temporary binder. Being able to paste readily at room temperature, Baka Snak helped to reduce the hydration rate of granules and thus minimize dry and wet spots in the dough. As a binder, it served to hold the product together during extrusion and initial frying. The binding and strengthening function was taken over by the amylose starch component when it had sufficiently hydrated, gelatinized and retrograded. In the absence of these cold-water dispersible starch derivatives, the fries tended to disintegrate and

explode before the amylose starch component was able to form a film and to function as described earlier.

'A' Clintose, a form of dextrose, was added to improve flavour and especially, to modify the browning of the fries. The amount of dextrose used can be varied to take account of the reducing sugar content of the potato granules and the colour desired.

Gelcarin M-100 and SeaCor SLC-2 which are seaweed gums, were equally effective binders that were the most suitable with F-T granules. Seaweed gums of the alginate type are extremely hydrophylic in nature and, hence, have a high water binding capacity, and are good binders (Glicksman 1969; McNeely 1959). The seaweed gum served to absorb and tie up free water in the dough, thus preventing separation and migration of free water while frying and allowing the product to retain moisture longer. However, guar gum, a galactomannan, appeared to be more compatible and effective than seaweed gums with the A-B granules. This could be due to the comparatively rapid hydration rate, and higher water binding and thickening properties of guar gum (Glicksman 1969). With either of the seaweed gums, the A-B dough was not sufficiently cohesive, and had a crumbly texture.

Sodium Carboxymethylcellulose (Na-CMC) and Hydroxypropylmethycellulose (Methocel) are cellulose-based binders (Batdorf 1959; Greminger et al. 1959) which have the ability to form oil resistant thermal films at relatively high temperatures (Glicksman 1959; Andres, 1976). The films are less prone to rupture due to migration of water during frying (Jadhav et al. 1976), and they reduce oil absorption (Scheffer and Klis 1965; Glicksman 1959; Jadhav et al. 1976). These additives served to minimize oil absorption, retain moisture and give a crunchy coating to the French

fries. Fries that contained Na-CMC alone tended to have rounded edges and a curled shape, and had high oil uptake. The product containing Methocel alone had a tough and leathery skin. A combination of both additives gave a product of acceptable oil content and good texture.

SUMMARY AND CONCLUSIONS

6.1. SEM STUDIES OF POTATO GRANULE PROCESSES.

The A-B and F-T processes differed essentially in their method of granulation. Different treatments of the potatoes were required in each process to bring about effective cell separation and, hence, granulation. SEM was effectively used to study different ultrastructural changes in potato cells through various steps of the processes. Potato cells appeared to be more prone to damage in the mash-mixing step of the A-B process than in the granulation step of the F-T process.

Granulation in the A-B process was accomplished during mash-mising by the recycled dry granules being pressed and embedded into newly cooked tissue, thereby separating the cells. Since the solubilization of cell binding material was reduced due to the precook treatment, cell separation might not be complete, leaving some unbroken lumps which would be discarded. Also, starch released when some of the cells were torn apart might cause the formation of aggregates, or might remain in the final product and cause glueyness on reconstitution.

In the F-T process, mashing separated the potato cells in the cooked tissue without much damage. Freezing and thawing of the potato mash increased the porosity of the CWs and caused partial separation of water from individual cells, thus resulting in rapid dehydration in the predrying step. Granulation of the predried cell aggregates was accomplished by the application of rigorous shear and compression to further separate individual cells from the aggregates with little cell damage.

The resultant A-B granules were largely round and more compact, with relatively smooth surfaces, while the F-T granules were mostly

angular, with considerable shrinkage, and their surface was covered with minute holes or craters which would allow faster rehydration. The A-B over-size particles appeared to consist of either unbroken tissue or agglomerates formed during mash-mixing, and amounted to as much as 5% or more of the total product. The discarded portion from the F-T process was generally much less, amounting to about 1% of the total output, and consisted mainly of unmashed tissue, or, if predrying was not properly controlled, some small agglomerates.

6.2. EFFECT OF THE PRECOOK TREATMENT IN THE F-T PROCESS.

Steam-cooked potatoes receiving a 20 min precook treatment at 70±1°C were firmer than those cooked without the pretreatment. The pre-treated cooked potatoes tended to remain intact, requiring greater mechanical force for subdivision into smaller aggregates during the short, but vigorous, mashing required in the F-T process. Mashing caused excessive cell damage, resulting in a gluey mash that could not be successfully processed into granules by the F-T process.

Precooked and cooked potatoes showed less solubilization of pectic substances (673.2±32.5 mg uronide/100 g dry matter) than did potatoes cooked without the precook treatment (1106±106.6 mg/100 g dry matter). Steam-cooking along appeared to solubilize all pectic substances, while one third of the pectin remained insolubile when precook treatment preceded steam-cooking. This suggested that the precook treatment rendered the pectic substances more resistant to further thermal degradation, thus decreasing the loss of intercellular cohesion and the rarefaction of CW brought about by subsequent cooking. Hence, precooked and cooked potato tissue was firmer than that which did not receive the pretreatment.

Electron photomicrographs showed that precooking gelatinized the

starch, which loosely filed the cells, while most of the CWs remained bound to one another. Since the binding force among the cells remained strong even after steam-cooking, cell separation was poor in the subsequent steps of the F-T process. This leads to the conclusion that, although precooking is of paramount importance to the success of the A-B process, it is detrimental to the efficiency of the F-T process.

6.3. MODEL STUDIES ON THE ROLE OF PME, CATIONS AND STARCH IN THE FIRMING EFFECT OF THE PRE-COOK TREATMENT OF POTATO TISSUE.

Pectin (as anhydrogalacturonic acid) amounted to 16% of the purified CW/ML preparations, and 55% of the pectin was esterified. The free carboxyl group content was 370 μM/g CW/ML dry matter. PME in CW/ML preparations accounted for 24% of the total tuber activity, showing an activity optimum at 60°C and pH 7.0.

During precooking at 65°C followed by cooling and final cooking, pectin solubilization was greater in the presence than in the absence of PME, whether Ca^{2+} was present or not. This suggested that PME activity may enhance pectin solubilization.

Added Ca^{2+} suppressed the solubilization of pectic substances in the CW/ML. The highest suppression was observed when Ca^{2+} equivalents corresponded stoichiometrically to pectin free carboxyl groups. Unlike Ca^{2+}, Mg^{2+} did not affect pectin solubilization. During precooking at 70°C, starch gelatinization occurred along with release of Ca^{2+}, which then formed Ca-bridges with free carboxyl groups on galacturonan. Cooling stabilized the Ca-bridges being formed and rendered the CW/ML pectic substances more resistant to further thermal degradation during final cooking.

Cooked potato tissue, precooked at 70 or 75°C in the presence of added Ca^{2+}, was significantly firmer (penetrometer reading of 751±47g-

force) than that precooked at 65°C (435±26g-force). The results showed that PME has a limited, and possibly negative, role in the firming of potato tissue. For maximum firmness, precooking should be done at a temperature sufficiently high to deactivate PME and gelatinize starch. A maximum quantity of Ca^{2+} from starch would then be available for pectin stabilization.

6.4. FURTHER DEVELOPMENT OF THE F-T PROCESS.

The batch F-T process was successfully modified to a semi-continuous one by connecting a cyclone collection system between the predrying, granulation and drying steps, and by varying air temperature and velocity, and stirrer speed. The information obtained in this experiment will be valuable in designing a continuous F-T processing line.

6.5. PHYSICOCHEMICAL CHANGES DURING AGING OF POTATO GRANULES.

Retrogradation of the starch in potato granules appeared to be the major physicochemical change during aging, giving rise to changes in other properties of potato granules. Upon prolonged storage, reversal of retrogradation and associated phenomena was observed.

Dissolution and subsequent reabsorption of salt crystals, found on surface of granules, might be involved in the reversal of retrogradation. These changes indicated that internal molecular rearrangement of starch influenced the rehydration properties of the granules and extrusion characteristics of the dough prepared for extruded French fries.

6.6 AN IMPROVED PROCESS FOR EXTRUDED FRENCH FRY PRODUCTION.

French fry mix consisting of 100 parts F-T granules, 5 parts Supro 630, 5 parts binder (a combination of Methocel, Na-CMC, Textaid, Baka snak, Crisp film, OK Ceri Gel, OK Pre Jel, and SeaCor), and 0.5

part each of dextrose and tetra sodium pyrophosphate, was found to be the most acceptable formula with respect to texture and taste of the extruded product. Automatic reconstitution, where the French fry mix and water were brought together in a small, continuous stream at a ratio of 1:2.3, was found to be most satisfactory for producing a uniform dough that lended itself well to extrusion and frying.

RECOMMENDATIONS FOR FURTHER WORK

The present investigation shed light on some properties of potato granules and the techniques for their production. It also highlighted a few areas in which additional work is required. The following are, therefore, recommended for further study:

1. It is believed that the freeze-thaw technique has commercial potential. However, an extensive pilot-plant scale study is necessary both to develop suitable equipment, and determine the economic feasibility of the process.

2. Calcium was shown to play an important role in tissue firming of potatoes during precooking. However, the role of starch must also be thoroughly investigated. It is possible, for example, that starch retrogrades during precooking and cooling, thus contributing to tissue firmness.

3. The present study indicated that PME activity may enhance pectin solubility. The exact nature of the enzyme and mechanisms of its actions should be studied in greater detail in order to further understand the changes occurring in potatoes during precooking and cooling.

4. The role of calcium in pectin solubilization and starch swelling has been investigated in this study and elsewhere. Further work on starch swelling, as affected by calcium in relation to the texture of cooked potatoes, may clarify the "swelling pressure" theory put forward by Reeve and co-workers (Reeve, 1954a,b,c; Potter et al., 1959).

5. A pilot scale study and consumer testing of the extruded French fries developed in this study are desirable to determine its commercial potential.

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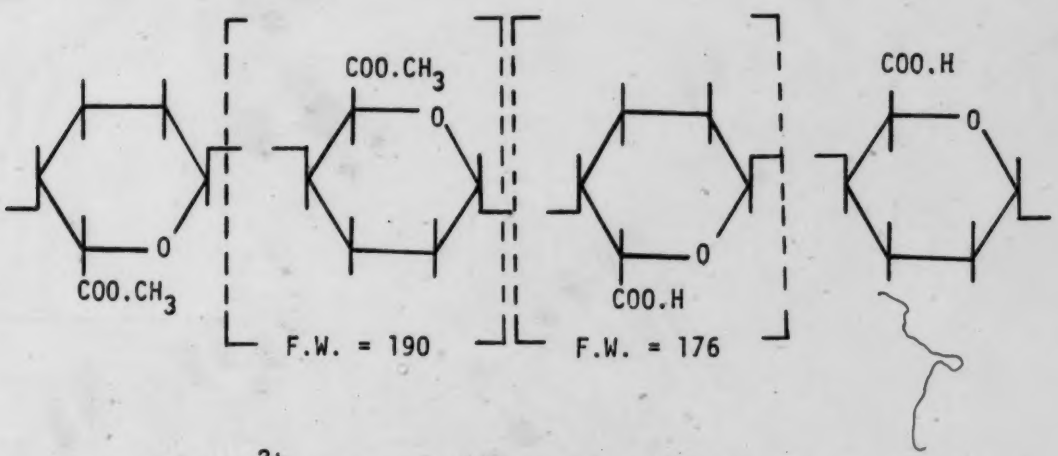
APPENDIX

Calculation of percent anhydrogalacturonic acid (% AGA) and degree of esterification (DE value) in pectins by the Cu^{2+} ion-exchange technique.



1. Each Cu^{2+} combines with two carboxylic groups, i.e. 1 µM (63.5 µg) Cu^{2+} combines with 2 µM COO^-.

2. If a µg Cu^{2+} combines with X µM of COO^- before saponification, then, $X = \frac{2a}{63.5}$ µM COO^-

Therefore, X = µM of acidic units in the galacturonan chain.

3. If b µg Cu^{2+} combines with Y M of COO^- after saponification then, $Y = \frac{2b}{63.5}$ µM COO^-

Therefore, Y = µM of total galacturonic units in the galacturonan chain.

4. $DE = \frac{\text{Total - Acidic}}{\text{Total}} \times 100\%$

Therefore, $DE = \frac{Y - X}{Y} \times 100\%$

5. Weight of acidic units in the chain = 176X µg and

Weight of esterified units = 190(Y - X) µg

Therefore, total weight of galacturonic units in the whole chain is $176X + 190(Y - X)$ µg and pectin ratio (as anhydrogalacturonic acid is

$$\frac{176X + 190(Y - X)\ \mu g}{\text{weight of sample in } \mu g}$$

6. % Pectin, as AGA = $\frac{176X + 190(Y - X)}{W} \times 100$

where a = µg Cu^{2+} bound before saponification

b = µg Cu^{2+} bound after saponification

$X = \frac{a}{31.75}$

$Y = \frac{b}{31.75}$

W = weight of sample in µg

Instrumental parameters for the atomic absorption spectrophotometer

Instrumental parameters	Cation				
	Cu^{2+}	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}
Lamp current (mA)	5	8	5	5	5
Photomultiplier voltage (V)	700	700	700	700	1000
Slit width (μ)	80	160	80	80	320
Wavelength (nm)	324.7	422.7	285.2	589.0	766.5
Fuel	acetylene	acetylene	acetylene	acetylene	acetylene
Fuel pressure (psi_g)	4.5	6.0	4.6	4.5	4.5
Oxidant	air	air	air	air	air
Oxidant pressure (psi_g)	8.0	10.0	8.0	7.0	7.0
Optimal range (ppm)	0.04-2.8	0.02-10	0.03-1	0.01-1	0.03-1
Sensitivity (ppm)	0.03	0.05	0.004	0.004	0.004

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry.
A-B	Add-Back
AGA	Anhydrogalacturonic acid.
BIV	Blue Iodine Value.
"Calgon"	Sodium hexametaphosphate.
Ca-starch	Calcium-starch.
CMC	Carboxymethylcellulose.
CRV	Carbazole Reaction Value.
CW(s)	Cell wall(s).
CW/ML	Cell wall and middle lamella.
d.m.	Dry matter.
d.m.b.	Dry matter basis.
E.U.('s)	Enzyme unit(s).
F-T	Freeze-Thaw
H-CW/ML	Hydrogen (cation free) cell wall and middle lamella.
H-starch	Hydrogen (cation free) starch.
M.C.%	Percent moisture content.
Methocel	Hydroxylpropyl methylcellulose.
ML	middle lamella.
Pipes	Piperazine-N, N'-bis [2-ethane sulphonic acid]
PME	Pectin methylesterase, E.C. 3.1.1.11.
PME unit (E.U.)	1 μM COO^- released per min at pH 7.5 at 30°C.
SEM	Scanning electron microscope (microscopy).
Tris	Tris (Hydroxymethyl) Aminomethane (THAM).
w.b.	Wet basis.
WHC	Water holding capacity.